S/079/61/031/003/003/013
B118/B207

AUTHORS: Shmonina, V. P., Temnikova, G. P., and Sokol'skiy, D. V.

TITLE: Catalytic reduction of aromatic nitro compounds. X. Effect of phenol hydroxyl upon the reduction kinetics of the nitro group in nitrobenzene derivatives

PERIODICAL: Zhurnal obshchey khimii, v. 31, no. 3, 1961, 743-749

TEXT: The present paper describes the effect exerted by the presence and position of phenol hydroxyl upon the reduction kinetics of the nitro group in isomeric nitrophenols in the presence of a nickel or platinum catalyst, i. e., in neutral or alkaline-aqueous alcoholic media. The phenol hydroxyl and ONa groups that were introduced into the nitro-compound molecule reduce its adsorption on both catalysts more intensively in ortho-position than in para-position where the reduction is greater than in meta-position. When the reaction is carried out on the skeleton nickel catalyst in an alkaline medium, the ONa group in the molecule of the nitro compound accelerates the reduction. Thus, the compounds studied may, with respect to the increase of reaction rate, be classified as follows: nitrobenzene, m-nitrophenolate,

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S/079/61/031/003/003/013
B118/B207

Catalytic reduction ...

p-nitrophenolate, o-nitrophenolate. On the platinum catalyst, however, the ONa group retards the reduction of the nitro compound, and the order of compounds is inverse with respect to the increase of reaction rate. In a neutral medium, the bond between hydrogen and platinum is less stable so that the position of phenol hydroxyl in the molecule exerts no essential influence upon the reaction rate. There are 6 figures, 4 tables, and 8 Soviet-bloc references.

ASSOCIATION: Kazakhskiy gosudarstvennyy universitet (Kazakh State University)

SUBMITTED: January 28, 1960

Card 2/2

TEMNIKOVA, L.F.

15

Absorption of phosphoric acid by the solonetzic soils (saline soils). L. F. Temnikova. *Uchenye Zapiski* [illegible] *Gosudarst. Univ. N. G. Chernyshevskogo*, [illegible] 1949, No. [illegible] [illegible] Solonetz soils absorb P_2O_5 [illegible] The B_1 horizon of the solonetzic soils does [illegible] differ greatly from the A horizon in its ability to bind P_2O_5, in spite of the large content of sesquioxides (R_2O_3). In this it differs from the red soils and from laterites. This is explained by the amphotytic behavior of R_2O_3 under the influence of the pH of the medium. Humus cannot bind P_2O_5 in large amts. Normal amts. of P fertilizers have a large effect on the solonetzic soils. The mixing of A and B_1 horizons has very little effect on the absorption of P_2O_5. Seven references. W. R. Henn

A S M - S L A METALLURGICAL LITERATURE CLASSIFICATION

SHKILEV, V.V.; TEMNIKOVA, L.V.

Case of importation of black rats into the city of Ussuriysk.
Izv.Irk.gos.nauch.-issl.protivochum.inst. 19:98-100 '58.
(MIRA 13:7)
(Ussuriysk--Rats)

COUNTRY : USSR
CATEGORY : Cultivated Plants. Cereals. M

ABS. JOUR. : RZhBiol., No. 1958, No. 104644

AUTHOR : Temnikova, N.
INST. : Academy of Sciences, Latvian SSR
TITLE : Experiments in Growing Corn in Latvia under the Meteorological Conditions of 1955.

ORIG. PUB. : Latv. PSR zinatnu Akad. vestis, Izv. AN Latv. SSR, No. 2, 57-62

ABSTRACT : The simplest method for the evaluation of adequate moisture supply is Selyaninov's "hydrothermal coefficient" (HTC). In regard to HTC, Latvian Republic has to be assigned to the zone of excessive precipitation. Experiments in growing corn were conducted at 13 points in the Republic. The milky stage of maturity came on 12 plots in the second and third 10-day period of September. For Osetinskaya variety, the weight of the green roughage varied from 377 to 1104 centners/ha. The relation of the

CARD: 1/2

COUNTRY :
CATEGORY :

M

ABS. JOUR. : RZhBiol., No. 23 1958, No. 104644

AUTHOR :
INST. :
TITLE :

ORIG. PUB. :

ABSTRACT : height of corn to the value of HTC was determined. This makes it possible to evaluate objectively one or another experimental point in regard to corn growing, and to evaluate the feasibility of the profitableness of corn production for green roughage in the individual rayons of Latvian SSR with the first approximation of climatic forecast. --O. V. Yakushkina

Card: 2/2

PHASE I BOOK EXPLOITATION SOV/4761

Kozyreva-Aleksandrova, L.S., and N.I. Temnikova

Radioaktivnyy izotop yoda J^{131} (Radioactive Isotope of Iodine J^{131})
Moscow, Atomizdat, 1960. 21 p. 15,000 copies printed.

Ed.: G.M. Pchelintseva; Tech. Ed.: N.A. Vlasova.

PURPOSE: This booklet is intended for scientific personnel working with radioisotopes, particularly for those interested in methods of extracting J^{131}.

COVERAGE: The authors note the increasingly wider application of radioistopes in science and industry, and review the theory of radioisotopes as developed in this century. The following are discussed briefly: chemical methods of extracting J^{131}, the extracting of J^{131} with the carrier from irradiated tellurium, methods of extracting carrier-free J^{131}, the extraction of J^{131} from neutron-irradiated tellurium, the applications of radioactive J^{131}, and safety

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Radioactive Isotope of Iodine J^{131} SOV/4761

engineering and technique in working with the radioactive iodine. No personalities are mentioned. There are 15 references, all Soviet.

TABLE OF CONTENTS: None given

AVAILABLE: Library of Congress (QD466.5I1Ks)

Card 2/2

JA/wrc/gmp
3-29-61

TEMNIKOVA, N.S.

Meteorological Abst.
Vol. 4 No. 3
March 1953
Part 2
Bibliography on
Frost and Frost
Forecasting

551.524.37(474)

4C-217

§ †Temnikova, Natdiia S., Tipizatsiia zamorozkov Evropeiskoĭ territorii Soiuza, ikh dlitel'nost' i povtoriaemost'. [Classification of frosts in European U.S.S.R., their duration and frequency.] *Meteorologiia i Gidrologiia*, 4(6):26–44, June 1938. 15 figs., 25 refs. DLC — On the basis of observations during 1891–1915, the author analyzes the conditions under which spring and autumn frosts form and establishes seven types of frost situations. The advection of cold (arctic or polar) air masses causes frosts. Their duration also depends on synoptic processes. Numerous charts illustrate synoptic situations, duration, frequency and distribution (seasonal and geographic) of frost. *Subject Headings:* 1. Frost distribution 2. Frost duration 3. Frost frequencies 4. Long period records 5. Synoptic conditions for frost 6. European U.S.S.R.

TEMNIKOVA,N.S., kandidat geograficheskikh nauk

A rare instance ofsurface inversion. Metero. i gidrol. no.2: 28-30 F '53. (MLRA 8:9)

1. Rostovskoye UGMS
(Atmospheric temperature)

TEMNIKOVA, N.S.

FEDOROV, Ye.Ye., professor; PREDTECHENSKIY, P.P.; BUCHINSKIY, I.Ye.; SEYANINOV, G.T., professor; BOSHNO, L.V.; ALISOV, B.P.; BIRYUKOV, N.N.; GAL'TSOV, A.P.; GRIGOR'YEV, A.A., akademik; EYGENSON, M.S., professor; MURETOV, N.S.; KHROMOV, S.P.; BOGDANOV, P.N.; LEBEDEV, A.N.; SOKOLOV, V.N.; YANISHEVSKIY, Yu.D.; SAMOYLENKO, V.S.; USMANOV, R.F.; CHUBUKOV, L.A.; TROTSENKO, S.Ya.; VANGENGEYM, G.Ya.; SOKOLOV, I.F.; STYRO, B.I.; TEMNIKOVA, N.S.; ISAYEV, E.A.; DMITRIYEV, A.A.; MALYUGIN, Ye.A.; LIEDEMAA, Ye.K.; SAPOZHNIKOVA, S.A.; RAKIPOVA, L.R.; POKROVSKAYA, T.V.; BAGDASARYAN, A.B.; ORLOVA, V.V.; RUBINSHTEYN, Ye.S., professor; MILEVSKIY, V.Yu.; SHCHERBAKOVA, Ye.Ya.; BOCHKOV, A.P.; ANAPOL'SKAYA, L.Ye.; DUNAYEVA, A.V.; UTESHEV, A.S.; RUDNEVA, A.V.; RUDENKO, A.I.; ZOLOTAREV, M.A.; NERSESYAN, A.G.; MIKHAYLOV, A.N.; GAVRILOV, V.A.; TSOMAYA, T.I.; DEVYATKOVA, A.M.; ZAVARINA, M.V.; SHMETER, S.M.; BUDYKO, M.I., professor.

Discussion of the report (in the form of debates) [of the current state climatological research and methods of developing it]. Inform. sbor.GUGMS no.3/4:26-154 '54. (MLRA 8:3)

1. Chlen-korrespondent Akademii nauk SSSR (for Fedorov). 2. Glavnaya geofizicheskaya observatoriya im. A.I.Voeykova (for Predtechenskiy, Lebedev, Yanishevskiy, Isayev, Rakipova, Pokrovskaya, Orlova, Rubinshteyn, Budyko, Shcherbakova, Anapol'skaya, Dunayeva, Rudneva, Gavrilov, Zavarina). 3. Ukrainskiy nauchno-issledovatel'skiy gidrometeorologicheskiy institut (for Buchinskiy).

(Continued on next card)

FEDOROV, Ye.Ye., professor; PREDTECHENSKIY, P.P., and others.

Discussion of the report (in the form of debates) [of the current state climatological research and methods of developing it]. Inform. sbor. GUGMS no.3/4:26-154 '54. (MIRA 8:3)
(Card 2)

4. Vsesoyuznyy institut rastenievodstva (for Selyaninov, Rudenko). 5. Bioklimaticheskaya stantsiya Kislovodsk (for Boshno). 6. Moskovskiy gosudarstvennyy universitet im. M.V.Lomonosova (for Alisov). 7. Ministerstvo putey soobshcheniya SSSR (for Biryukov). 8. Institut geografii Akademii nauk SSSR (for Gal'tsov, Grigor'yev). 9. Geofizicheskaya komissiya Vsesoyuznogo geograficheskogo obshchestva (for Eygenson). 10. Ministerstvo elektrostantsiy i elektropromyshlennosti SSSR (for Muretov). 11. Leningradskiy gosudarstvennyy universitet im. A.A.Zhdanova (for Khromov). 12. TSentral'nyy nauchno-issledovatel'skiy gidrometeorologicheskiy arkhiv (for Sokolov, Zolotarev). 13. Gosudarstvennyy okeanograficheskiy institut (for Samoylenko). 14. TSentral'nyy institut prognozov (for Usmanov, Sapozhnikova). 15. Institut geografii Akademii nauk SSSR i TSentral'nyy institut kurortologii (for Chubukov). 16. Nauchno-issledovatel'skiy institut imeni Sechenova, Yalta (for Trotsenko). 17. Arkticheskiy nauchno-issledovatel'skiy institut (for Vangengeym).

(Continued on next card)

FEDOROV, Ye.Ye., professor; PREDTECHENSKIY, P.P., and others.

Discussion of the report (in the form of debates) [of the current state of climatological research and methods of developing it]. Inform.sbor. GUGMS no.3/4:26-154 '54. (Card 3) (MLRA 8:3)

18. Dal'nevostochnyy nauchno-issledovatel'skiy gidrometeorologicheskiy institut (for Sokolov). 19. Institut geologii i geografii Akademii nauk Litovskoy SSR (for Styro). 20. Rostovskoe upravlenie gidrometsluzhby (for Temnikova). 21. Morskoy gidrofizicheskiy Institut Akademii nauk SSSR (for Dmitriyev). 22. Vsesoyuznyy institut rasteniyevodstva (for Malyugin). 23. Akademiya nauk Estonskoy SSR (for Liedemaa). 24. Akademiya nauk Armyanskoy SSR (for Bagdasaryan). 25. Leningradskiy gidrometeorologicheskiy institut (for Milevskiy).

(Continued on next card)

FEDOROV, Ye.Ye., professor; PREDTECHENSKIY, P.P., and others.

Discussion of the reports (in the form of debates) [of the current state climatological research and methods of developing it]. Inform.sbor. GUGMS no.3/4:26-154 '54. (Card 4) (MLRA 8:3)

26. Gosudarstvennyy gidrologicheskiy institut (for Bochkov). 27. Kazakhskiy nauchno-issledovatel'skiy gidrometeorologicheskiy institut (for Uteshev). 28. Upravlenie gidrometsluzhby Armyanskoy SSR (for Nersesyan). 29. Leningradskoye upravleniye gidrometsluzhby (for Mikhaylov, Devyatkova). 30. Tbilisskiy gosudarstvennyy universitet (for Tsomaya). 31. TSentral'naya aerologicheskaya observatoriya (for Shmeter).
(Climatology)

TEMNIKOVA, N.S.

AID P - 1433

Subject : USSR/Meteorology and Hydrology

Card 1/1 Pub. 71-a - 7/23

Author : Temnikova, N. S., Kandidat of Geogr. Sciences

Title : Dust storms in the Stalinograd district

Periodical : Met. i gidro., 1, 31-32, Ja - F 1955

Abstract : Statistical data are given of dust storms with a wind volocity of 12-15m/sec. from an analysis of observations taken from 1936 to 1950. Measures of protection are suggested and a table given of these storms by months observed at 7 stations for 1948 and 1949. One Russian reference

Institution: Main Administration of the Hydrometeorological Service at the Council of Ministers of the USSR

Submitted : No date

TEMNIKOVA, M. S.

AID P - 3182

Subject : USSR/Meteorology

Card 1/1 Pub. 71-a - 9/23

Author : Temnikova, M. S.

Title : Early frost on ploughed land and meadows

Periodical : Met. i. gidr., 5, 38-40, S/O 1955

Abstract : The possibility of forecasting early and late frost following 10 year observations made in Latvia is discussed. The freezing of corn at temperatures of -2°C is reported. Diagrams show the difference in temperatures of air, ploughed earth and soil covered with grass. Four diagrams.

Institution : None

Submitted : No date

14-57-6-12148

Translation from: Referativnyy zhurnal, Geografiya, 1957, Nr 6, p 67 (USSR)

AUTHOR: Temnikova, N. S.

TITLE: Frost Danger in Various Forms of Hilly Regions (Morozoopasnost' razlichnykh form kholmistogo rel'yefa)

PERIODICAL: Izv. AN LatvSSR, 1956, Nr 9, pp 75-83

ABSTRACT: A microclimatic survey was carried out simultaneously at 13 points in the northeastern part of the Vidzemskaya vozvyshennost' (upland) from May 6 to June 11, 1954, during the period of the spring frosts. Results of the observations have shown that average minimum temperature (at an 0.5 m level) was 2° or 3° higher on the hill summits than in the adjacent valleys. These values were smaller on slopes than on hilltops, being only from 0.2° to 0.4°, and reached 1° only on

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Frost Danger in Various Forms (Cont.)

the steepest slopes. The greatest difference between minimum temperatures in the valleys and on the summits, reaching 4° or 5° and even 6°, was observed during the periods of cold advection; during warm advection these differences decreased sharply. The extent of differences between these values depends also on the clouds and on the wind velocity, but steepness of a slope and its exposure have no effect on it. Regardless of the weather, the average minimum temperatures are lowest in the valleys and highest on the summits. Thermal relations over the slopes, valleys, and summits are substantially different during the periods of hot and cold advection. Regardless of whether the weather is clear, overcast or windy, the temperature differences are considerably smaller during the periods of warm advection than during the periods of cold advection.

I. D.

Card 2/2

TEMNIKOVA, M.S.

Meteorological conditions during the solar eclipse of June 30, 1954, in Latvian S.S.R. Biul.VAGO no.20:12-18 '57. (MLRA 10:8)

1.Rizhskaya geofizicheskaya observatoriya.
(Latvia--Meteorology--Observations)
(Eclipses, Solar--1954)

SOV/5o-59-5-11/22

3(7)
AUTHOR: Temnikova, N. S.

TITLE: Methods of Studying the Microclimate (O metodakh izucheniya mikroklimata)

PERIODICAL: Meteorologiya i gidrologiya, 1959, Nr 5, pp 45 - 48 (USSR)

ABSTRACT: The agroclimatic handbooks, the program of which contains a section on the microclimate, need microclimatic corrections. Up to now, the principal method of obtaining these mean microclimatic corrections has been the method of the analysis of so-called background (fonovyy) charts. This method has, however, some relevant shortcomings. It is shown here that reliable microclimatic corrections for the different meteorological elements can only be obtained at present by means of microclimatic special surveys in the different regions of the USSR. The experience of the Rizhskaya gidrometeorologicheskaya observatoriya (Riga Hydrometeorological Observatory) of the UGMS Latv. SSR (Hydrometeorological Service Administration of the Latvian SSR) shows that such surveys can be organized very easily with the forces of the hydrometeorological stations working at present. In fall 1957, the UGMS of the Estonian, Lithuanian and Latvian SSR began to carry out a

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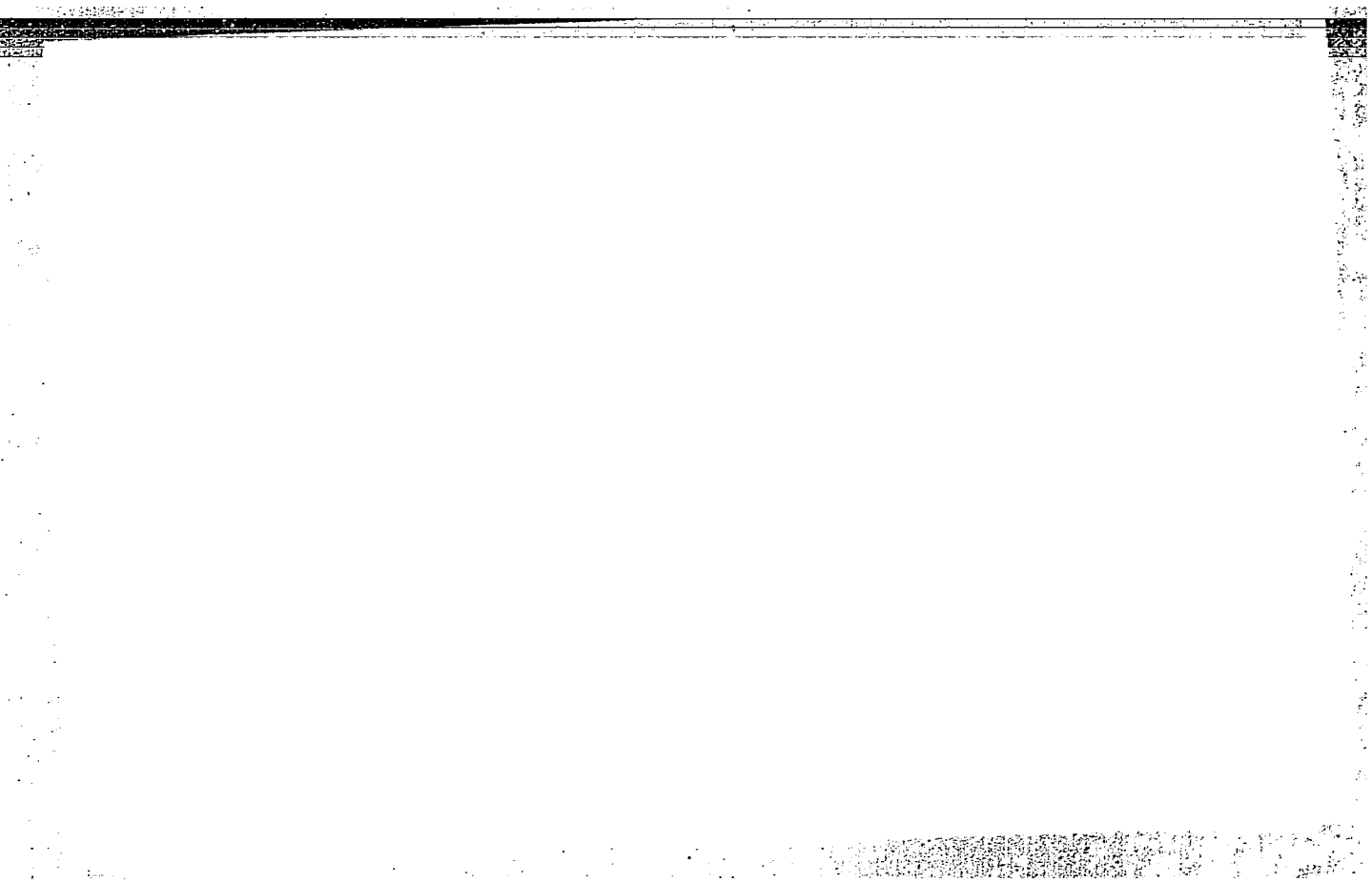
number of such surveys in the Baltics. First of all, the influence of the different forms of hill country on the climate is to be clarified. The execution of these surveys is described here in short. In the descriptions of the MCP (microclimatic points), the character of the vegetation and soil, the moisture content of the surface of the soil, the steepness and illumination of the slope, the relative superelevation above the bottom of the valley, and possibly the profile of the slope, should be indicated. The observations must be made in fall, from September 20 until the time when the mean diurnal air temperature continuously exceeds 5°, and in spring, from April 16 to June 15. According to the program described here, the regions of the Vidzem and Kurzem Elevations were investigated microclimatically in fall 1957 and in the warm period of 1958. To check the data obtained, analogous surveys were carried out by the method given here at the hydrometeorological station of Saldus on the Kurzem Elevation. These data were evaluated by L. M. Fonina. The results were in full conformity with those obtained before. This fact shows that there are certain rules in the distribution of microclimatic corrections for the same relief forms in the same region. The microclimatic investigations of the moisture content of the soil are theoreti-

cally very interesting and very important to practice. In this connection, it would be convenient to complete the survey program of 1958 by measurements of the soil moisture content in the upper horizon and in the arable horizon. There are 7 Soviet references.

TEMNIKOVA, Natal'ya Sergeyevna; DROZDOV, O.A., prof., red.; USHAKOVA, T.V., red.; SERGEYEV, A.N., tekhn.red.

[Climate of the Northern Caucasus and adjacent steppes] Klimat Severnogo Kavkaza i prilezhashchikh stepei. Pod red. O.A.Drozdova. Leningrad, Gidrometeor.izd-vo, 1959. 367 p. (MIRA 13:2)
(Caucasus, Northern--Climate)



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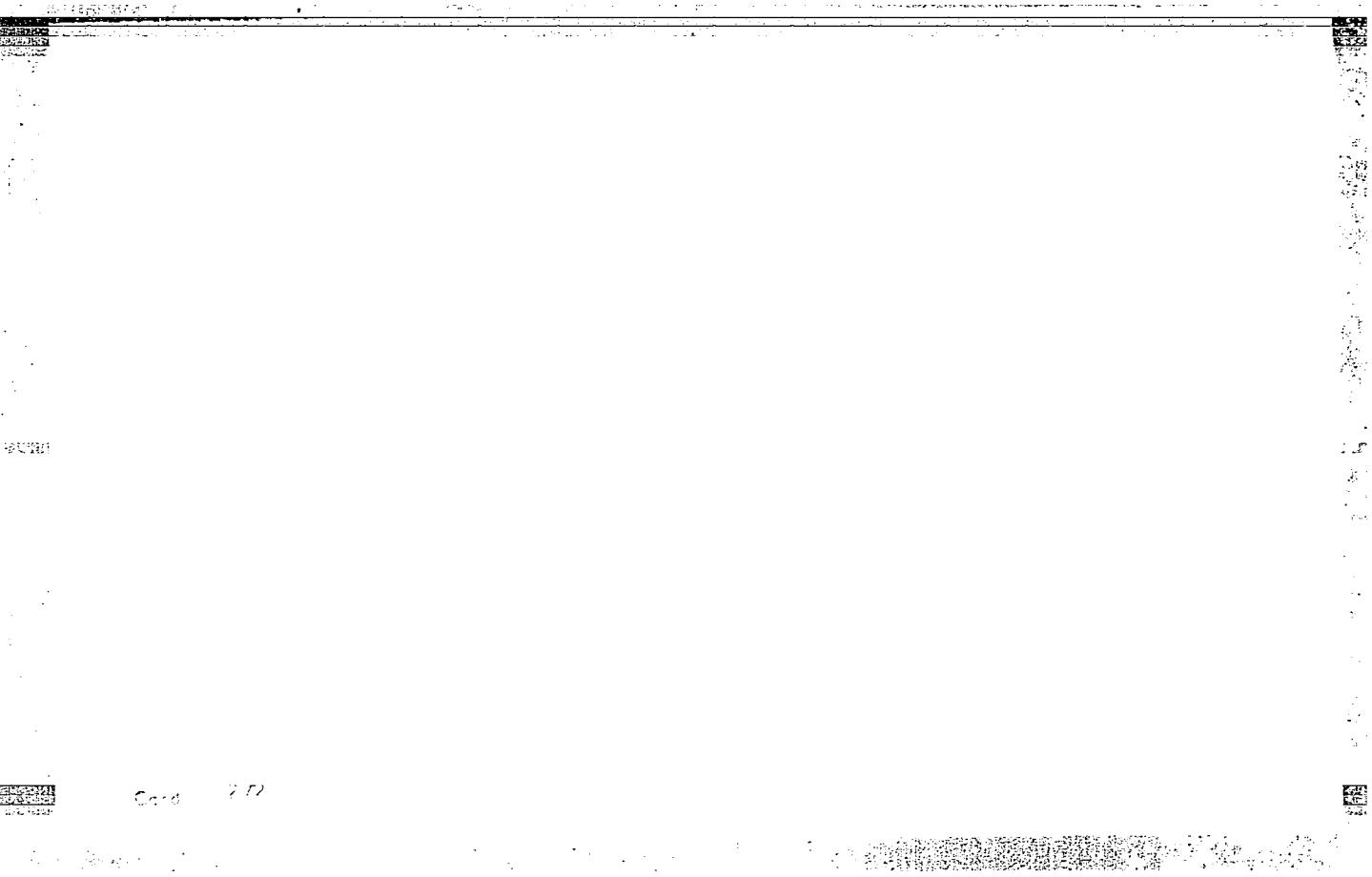
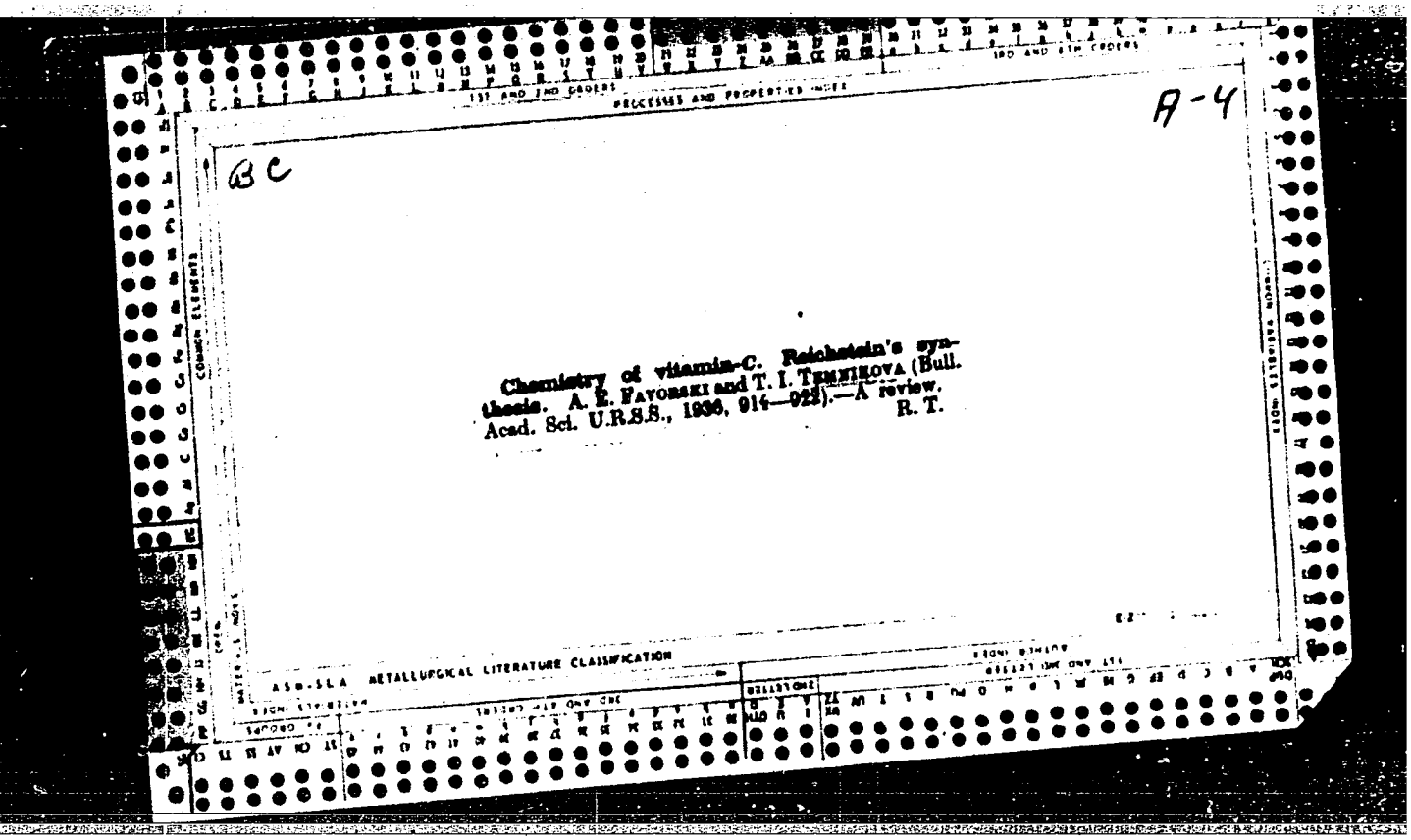


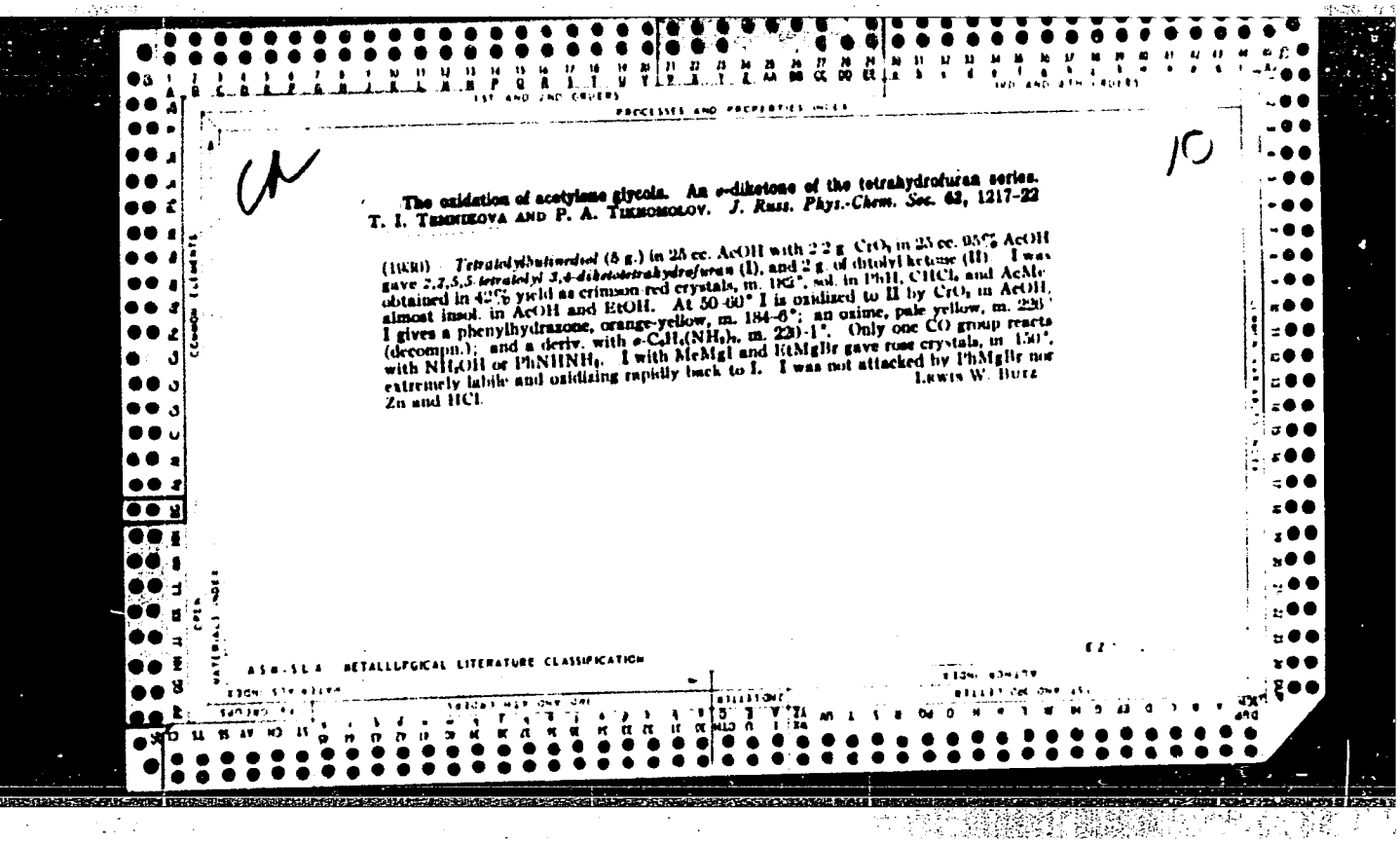
APPROVED FOR RELEASE: 07/16/2001 CIA-RDP86-00513R001755220014-4"

TEMNIKOVA, R. T.

"Experimental Investigations of the Characteristics of Ultrasound Propagation in Suspensions."

report presented at the 6th Sci. Conference on the Application of Ultrasound in the Investigation of Matter, 3-7 Feb 1958, organized by Min. of Education RSFSR and Moscow Oblast Pedagogic Inst. im N. K. Krupskaya.

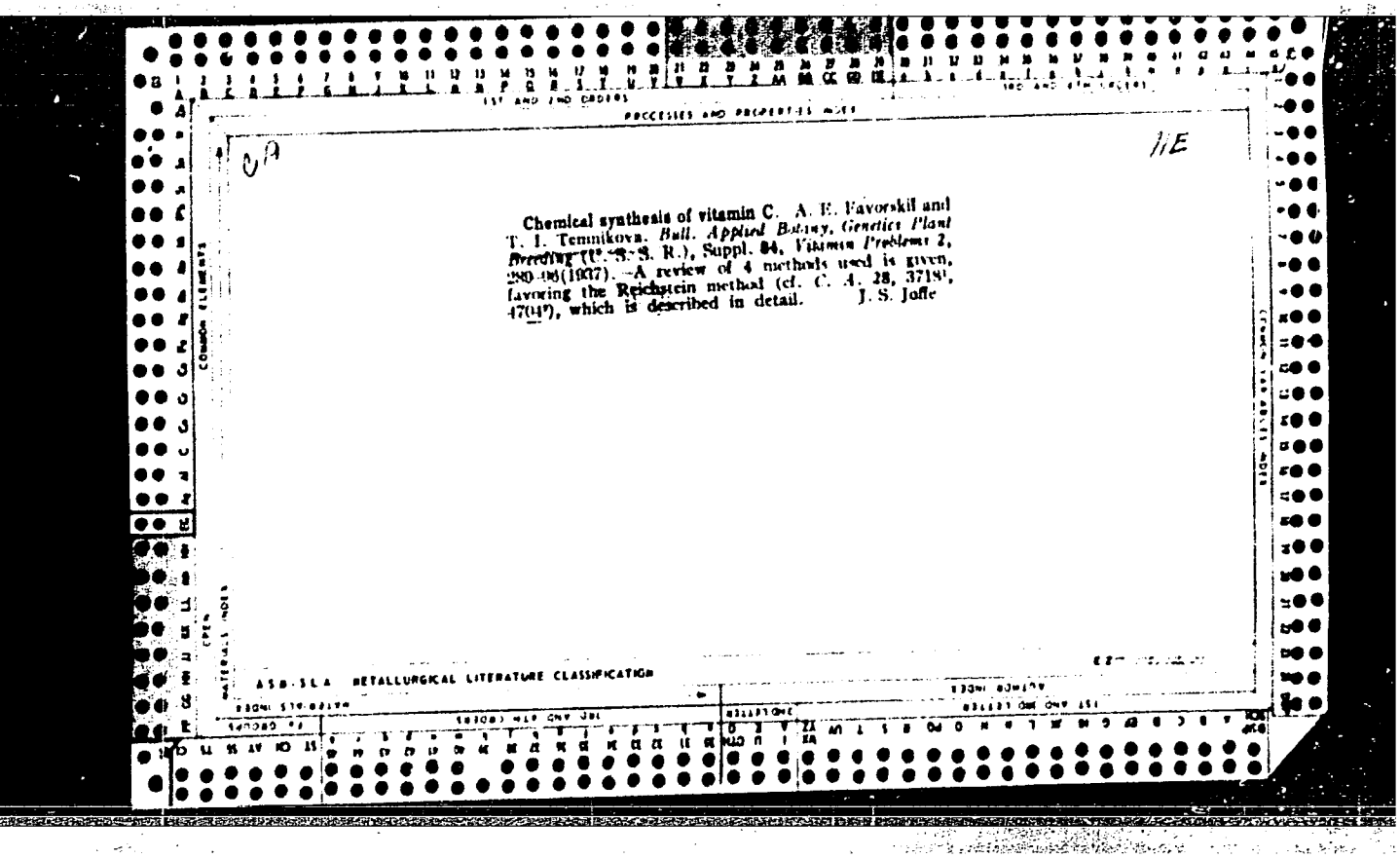




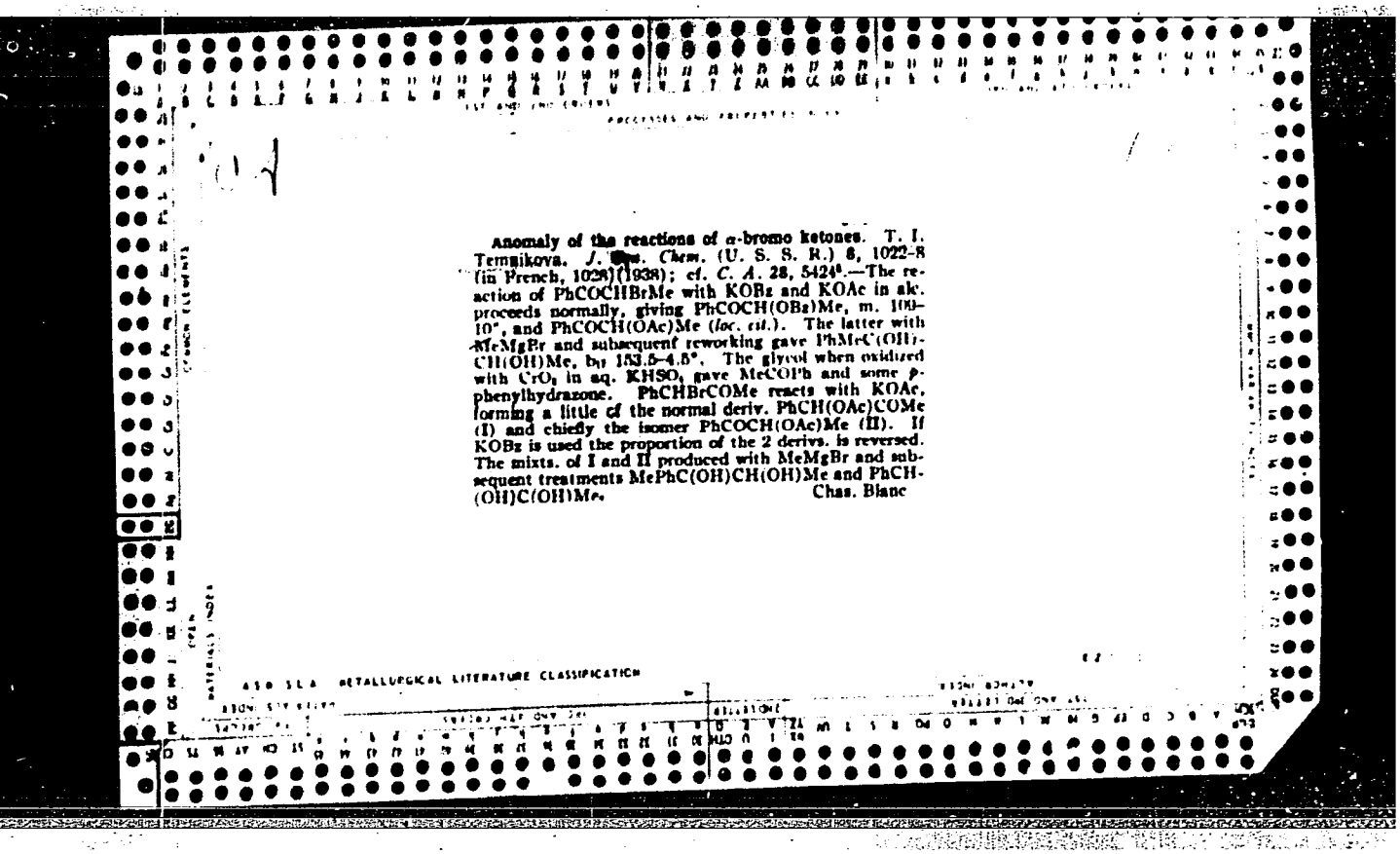
The oxidation of acetylene glycols. An α-diketone of the tetrahydrofuran series.
T. I. Temnikova and P. A. Tikhomolov. *J. Russ. Phys.-Chem. Soc.* 62, 1217-22

(1930). *Tetraisobutinediol* (5 g.) in 25 cc. AcOH with 2.2 g. CrO_3 in 25 cc. 95% AcOH gave *2,2,5,5-tetraisobutyl-3,4-dihydroxytetrahydrofuran* (I), and 2 g. of diisobutyl ketone (II). I was obtained in 42% yield as crimson-red crystals, m. 182°, sol. in PhH, $CHCl_3$, and AcMe almost insol. in AcOH and EtOH. At 50-60° I is oxidized to II by CrO_3 in AcOH. I gives a phenylhydrazone, orange-yellow, m. 184-6°; an oxime, pale yellow, m. 228° (decompn.); and a deriv. with o-$C_6H_4(NH_2)_2$, m. 223-1°. Only one CO group reacts with NH_2OH or $PhNHNH_2$. I with MeMgI and EtMgBr gave rose crystals, m. 150°, extremely labile and oxidizing rapidly back to I. I was not attacked by PhMgBr nor Zn and HCl.

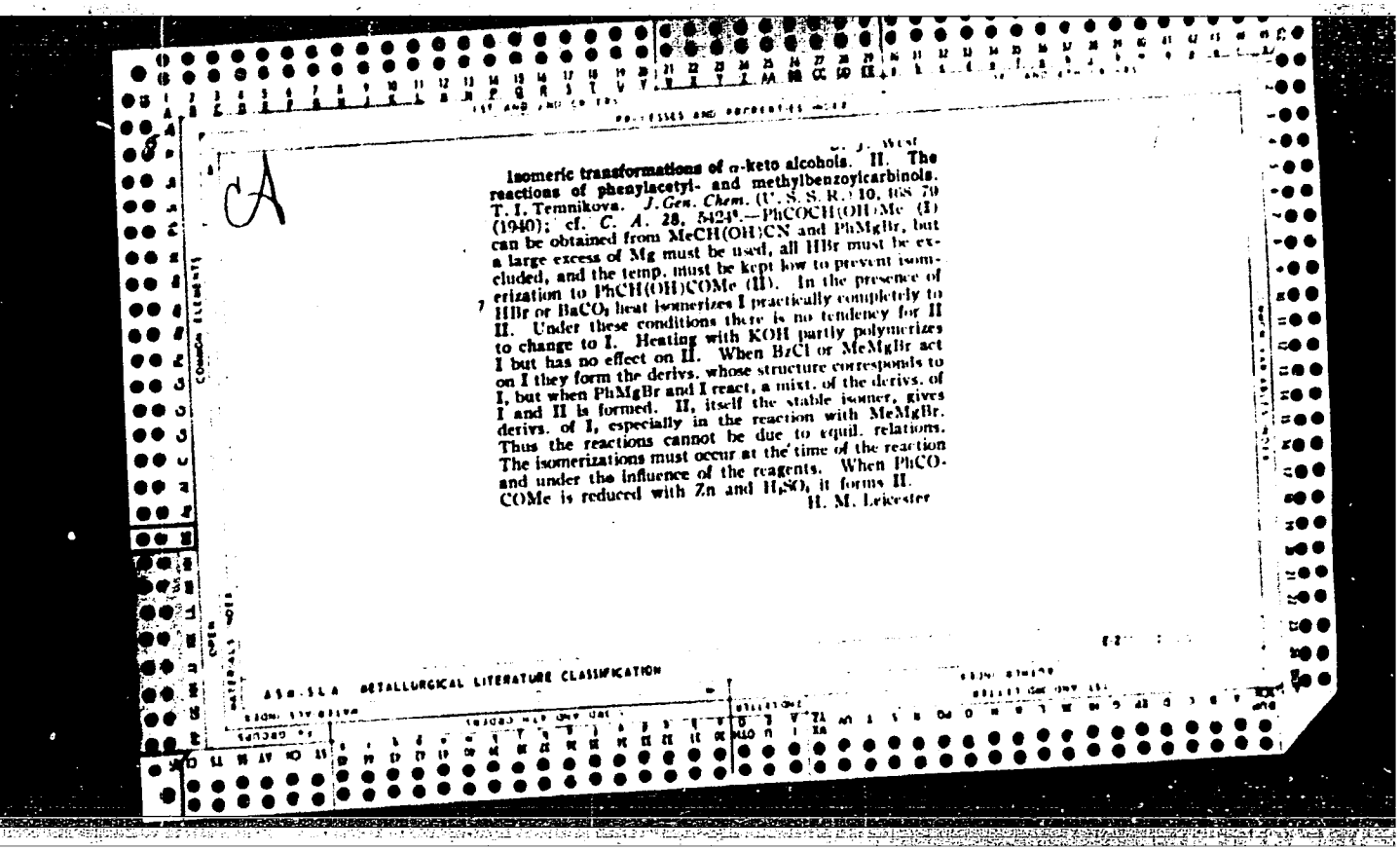
Lewis W. Butz



Chemical synthesis of vitamin C. A. E. Favorskii and T. I. Temnikova. *Bull. Applied Botany, Genetics Plant Breeding* (U. S. S. R.), Suppl. 84, *Vitamin Problems* 2, 280-96(1937). —A review of 4 methods used is given, favoring the Reichstein method (cf. C. A. 28, 3718[1], 4704[9]), which is described in detail. J. S. Joffe



Anomaly of the reactions of α-bromo ketones. T. I. Temnikova. *J. Gen. Chem.* (U. S. S. R.) 8, 1022–8 (in French, 1028)(1938); cf. *C. A.* 28, 5424[8].—The reaction of PhCOCHBrMe with KOBz and KOAc in alc. proceeds normally, giving PhCOCH(OBz)Me, m. 109–10°, and PhCOCH(OAc)Me (*loc. cit.*). The latter with MeMgBr and subsequent reworking gave PhMeC(OH)-CH(OH)Me, b_{15} 153.5–4.5°. The glycol when oxidized with CrO_3 in aq. $KHSO_4$ gave MeCOPh and some *p*-phenylhydrazone. PhCHBrCOMe reacts with KOAc, forming a little of the normal deriv. PhCH(OAc)COMe (I) and chiefly the isomer PhCOCH(OAc)Me (II). If KOBz is used the proportion of the 2 derivs. is reversed. The mixts. of I and II produced with MeMgBr and subsequent treatments MePhC(OH)CH(OH)Me and PhCH-(OH)C(OH)Me. Chas. Blanc

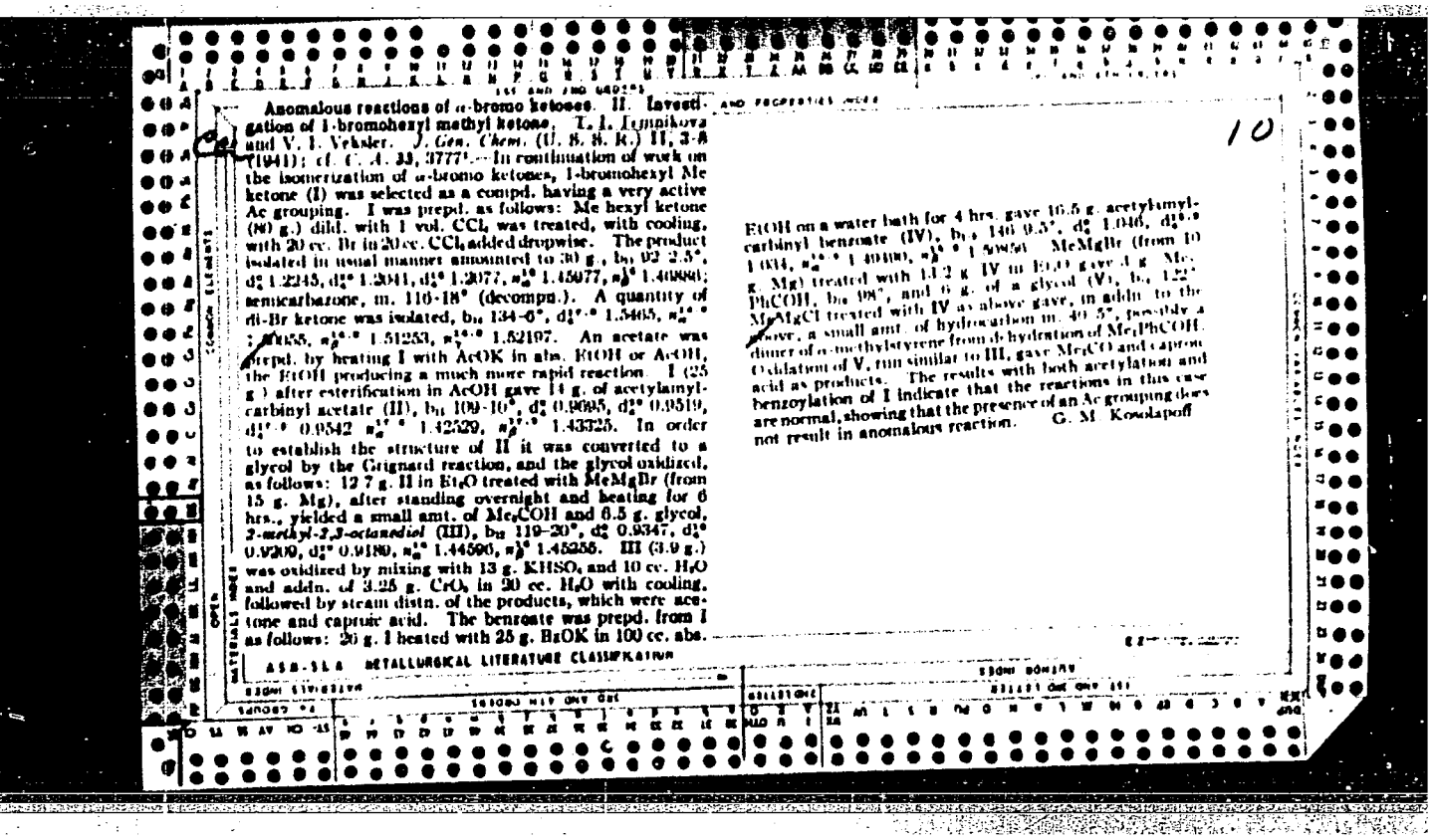


CA

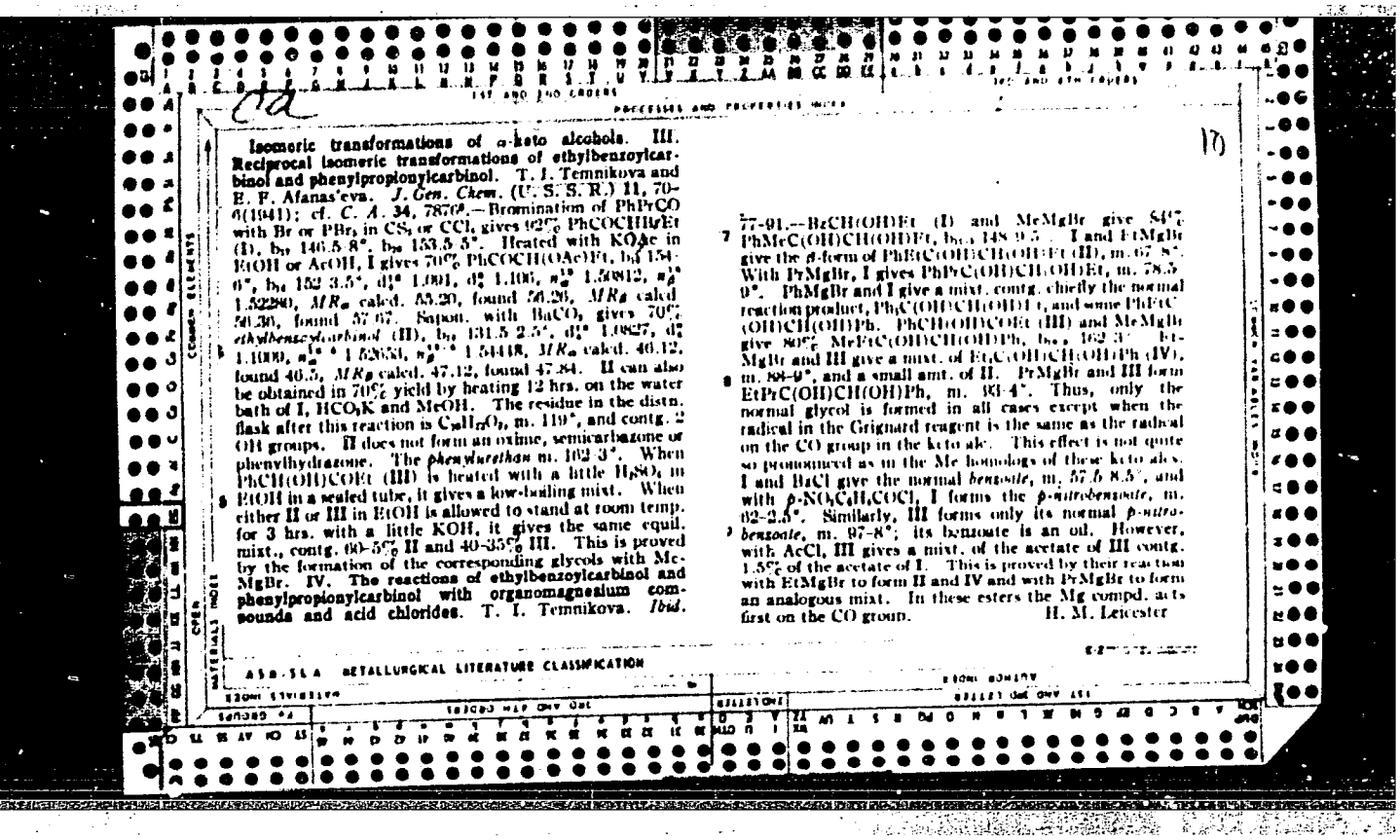
Isomeric transformations of α-keto alcohols. II. The reactions of phenylacetyl- and methylbenzoylcarbinols. T. I. Temnikova. *J. Gen. Chem.* (U. S. S. R.) 10, 168–70 (1940); cf. *C. A.* 28, 5424⁹.—PhCOCH(OH)Me (I) can be obtained from MeCH(OH)CN and PhMgBr, but a large excess of Mg must be used, all HBr must be excluded, and the temp. must be kept low to prevent isomerization to PhCH(OH)COMe (II). In the presence of HBr or $BaCO_3$ heat isomerizes I practically completely to II. Under these conditions there is no tendency for II to change to I. Heating with KOH partly polymerizes I but has no effect on II. When BzCl or MeMgBr act on I they form the derivs. whose structure corresponds to I, but when PhMgBr and I react, a mixt. of the derivs. of I and II is formed. II, itself the stable isomer, gives derivs. of I, especially in the reaction with MeMgBr. Thus the reactions cannot be due to equil. relations. The isomerizations must occur at the time of the reaction and under the influence of the reagents. When PhCOCOMe is reduced with Zn and H_2SO_4 it forms II.

H. M. Leicester

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION



Anomalous reactions of α-bromo ketones. II. Investigation of 1-bromohexyl methyl ketone. T. I. Temnikova and V. I. Veksler. *J. Gen. Chem.* (U. S. S. R.) 11, 3-8 (1941); cf. C. A. 33, 3777[1]. — In continuation of work on the isomerization of α-bromo ketones, 1-bromohexyl Me ketone (I) was selected as a compd. having a very active Ac grouping. I was prepd. as follows: Me hexyl ketone (80 g.) dild. with 1 vol. CCl_4 was treated, with cooling, with 20 cc. Br in 20 cc. CCl_4 added dropwise. The product isolated in usual manner amounted to 30 g., b_{11} 92-2.5°, d_4^{20} 1.2245, d_4^{15} 1.2041, d_4^{0} 1.2077, n_{α}^{20} 1.45977, n_{β}^{20} 1.46988; semicarbazone, m. 110-18° (decompn.). A quantity of di-Br ketone was isolated, b_{11} 134-6°, d_4^{20} 1.5465, n_{α}^{20} [illegible], n_{β}^{20} 1.51253, n_{γ}^{20} 1.52197. An acetate was prepd. by heating I with AcOK in abs. EtOH or AcOH, the EtOH producing a much more rapid reaction. I (25 g.) after esterification in AcOH gave 14 g. of acetylamylcarbinyl acetate (II), b_{11} 109-10°, d_4^{20} 0.9695, d_4^{15} 0.9519, d_4^{0} 0.9542 n_{α}^{17} 1.42529, n_{β}^{17} 1.43325. In order to establish the structure of II it was converted to a glycol by the Grignard reaction, and the glycol oxidized, as follows: 12.7 g. II in Et_2O treated with MeMgBr (from 15 g. Mg), after standing overnight and heating for 6 hrs., yielded a small amt. of Me_3COH and 6.5 g. glycol, *2-methyl-2,3-octanediol* (III), b_{11} 119-20°, d_4^{20} 0.9347, d_4^{15} 0.9200, d_4^{0} 0.9180, n_{α}^{20} 1.44590, n_{β}^{20} 1.45255. III (3.9 g.) was oxidized by mixing with 13 g. $KHSO_4$ and 10 cc. H_2O and addn. of 3.25 g. CrO_3 in 20 cc. H_2O with cooling, followed by steam distn. of the products, which were acetone and caproic acid. The benzoate was prepd. from I as follows: 20 g. I heated with 25 g. BzOK in 100 cc. abs. EtOH on a water bath for 4 hrs. gave 16.5 g. acetylamylcarbinyl benzoate (IV), b_{11} 140-0.5°, d_4^{20} 1.046, d_4^{15} 1.0434, n_{α}^{20} 1.49180, n_{β}^{20} 1.50050. MeMgBr (from 10 g. Mg) treated with 14.2 g. IV in Et_2O gave 4 g. Me_2PhCOH, b_{11} 98°, and 6 g. of a glycol (V), b_{11} 122°. $MeMgCl$ treated with IV as above gave, in addn. to the glycol, a small amt. of hydrocarbon m. 40-5°, possibly a dimer of α-methylstyrene from dehydration of Me_2PhCOH. Oxidation of V, run similar to III, gave Me_2CO and caproic acid as products. The results with both acetylation and benzoylation of I indicate that the reactions in this case are normal, showing that the presence of an Ac grouping does not result in anomalous reaction. G. M. Kosolapoff



Isomeric transformations of α-keto alcohols. III. Reciprocal isomeric transformations of ethylbenzoylcarbinol and phenylpropionylcarbinol. T. I. Temnikova and E. F. Afanas'eva. *J. Gen. Chem.* (U. S. S. R.) 11, 70-6(1941); cf. *C. A.* 34, 7870⁸.—Bromination of PhPrCO with Br or PBr_3 in CS_2 or CCl_4 gives 92% PhCOCHBrEt (I), b_{10} 146.5-8°, b_{16} 153.5-5°. Heated with KO_2Ac in EtOH or AcOH, I gives 70% PhCOCH(OAc)Et, b_4 154-6°, b_{16} 152-3.5°, d_4^{19} 1.091, d_4^{20} 1.105, n_D^{19} 1.50812, n_D^{20} 1.50280, MR_D calcd. 55.20, found 56.26, MR_β calcd. 56.30, found 57.07. Saponification with $BaCO_3$ gives 70% *ethylbenzoylcarbinol* (II), b_{16} 131.5-2.5°, d_4^{19} 1.0827, d_4^{20} 1.1000, n_D^{19} 1.52650, $n_D^{19.5}$ 1.54448, MR_D calcd. 46.12, found 46.5, MR_β calcd. 47.12, found 47.84. II can also be obtained in 70% yield by heating 12 hrs. on the water bath of I, HCO_2K and MeOH. The residue in the distn. flask after this reaction is $C_{18}H_{18}O_3$, m. 119°, and contg. 2 OH groups. II does not form an oxime, semicarbazone or phenylhydrazone. The *phenylurethan* m. 102-3°. When PhCH(OH)COEt (III) is heated with a little H_2SO_4 in EtOH in a sealed tube, it gives a low-boiling mixt. When either II or III in EtOH is allowed to stand at room temp. for 3 hrs. with a little KOH, it gives the same equil. mixt., contg. 60-5% II and 40-35% III. This is proved by the formation of the corresponding glycols with MeMgBr. IV. **The reactions of ethylbenzoylcarbinol and phenylpropionylcarbinol with organomagnesium compounds and acid chlorides.** T. I. Temnikova. *Ibid.* 77-91.—BzCH(OH)Et (I) and MeMgBr give 84% PhMeC(OH)CH(OH)Et, $b_{16.5}$ 148-9.5°. I and EtMgBr give the β-form of PhEtC(OH)CH(OH)Et (II), m. 67-8°. With PrMgBr, I gives PhPrC(OH)CH(OH)Et, m. 78.5-9°. PhMgBr and I give a mixt. contg. chiefly the normal reaction product, $Ph_2C(OH)CH(OH)Et$, and some PhEtC(OH)CH(OH)Ph. PhCH(OH)COEt (III) and MeMgBr give 80% MePhC(OH)CH(OH)Ph, b_{16} 162-3°. EtMgBr and III give a mixt. of $Et_2C(OH)CH(OH)Ph$ (IV), m. 88-9°, and a small amt. of II. PrMgBr and III form EtPrC(OH)CH(OH)Ph, m. 93-4°. Thus, only the normal glycol is formed in all cases except when the radical in the Grignard reagent is the same as the radical on the CO group in the keto alc. This effect is not quite so pronounced as in the Me homologs of these keto alcs. I and BzCl give the normal *benzoate*, m. 57.5-8.5°, and with *p*-$NO_2C_6H_4COCl$, I forms the *p-nitrobenzoate*, m. 92-2.5°. Similarly, III forms only its normal *p-nitrobenzoate*, m. 97-8°; its benzoate is an oil. However, with AcCl, III gives a mixt. of the acetate of III contg. 1.5% of the acetate of I. This is proved by their reaction with EtMgBr to form II and IV and with PrMgBr to form an analogous mixt. In these esters the Mg compd. acts first on the CO group. H. M. Leicester

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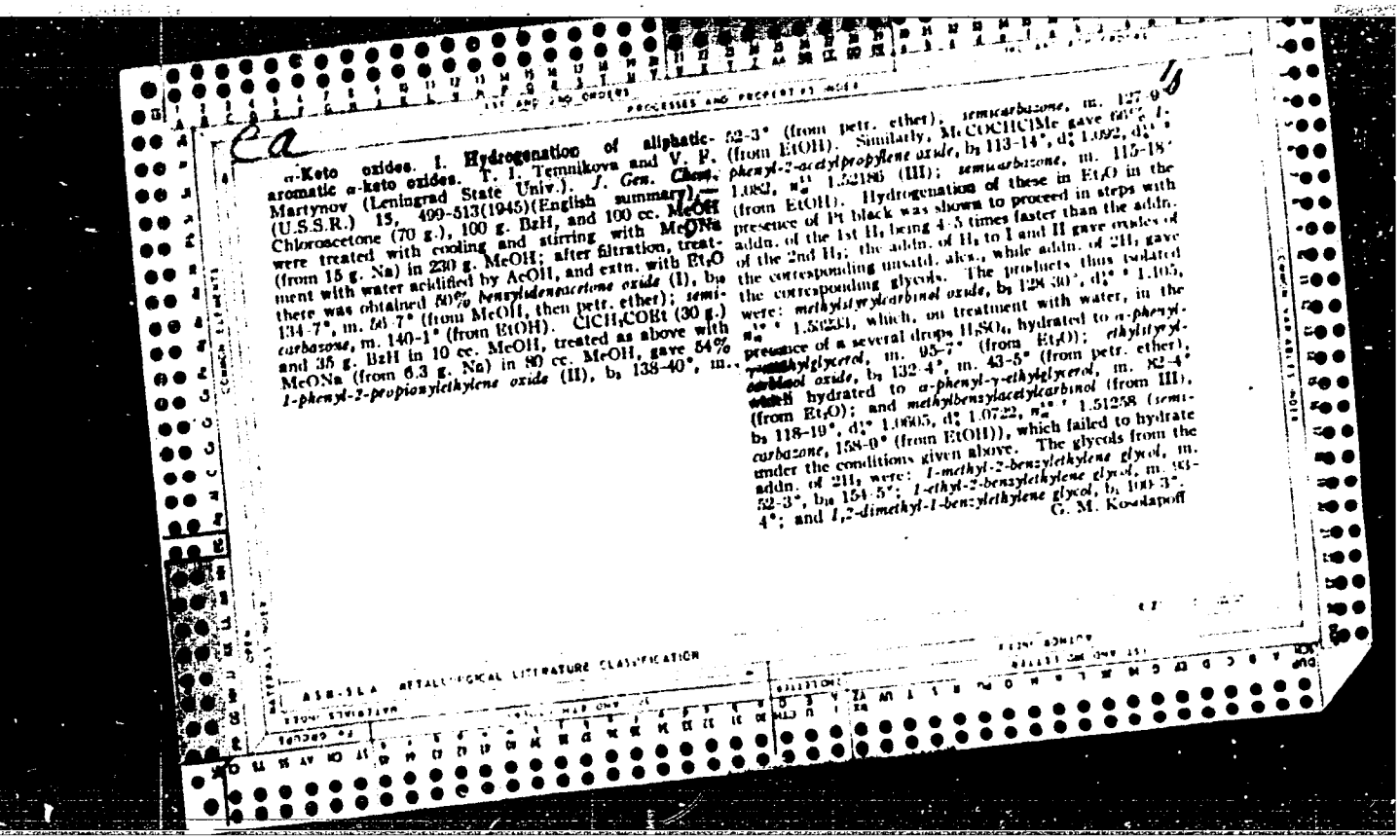


Ca

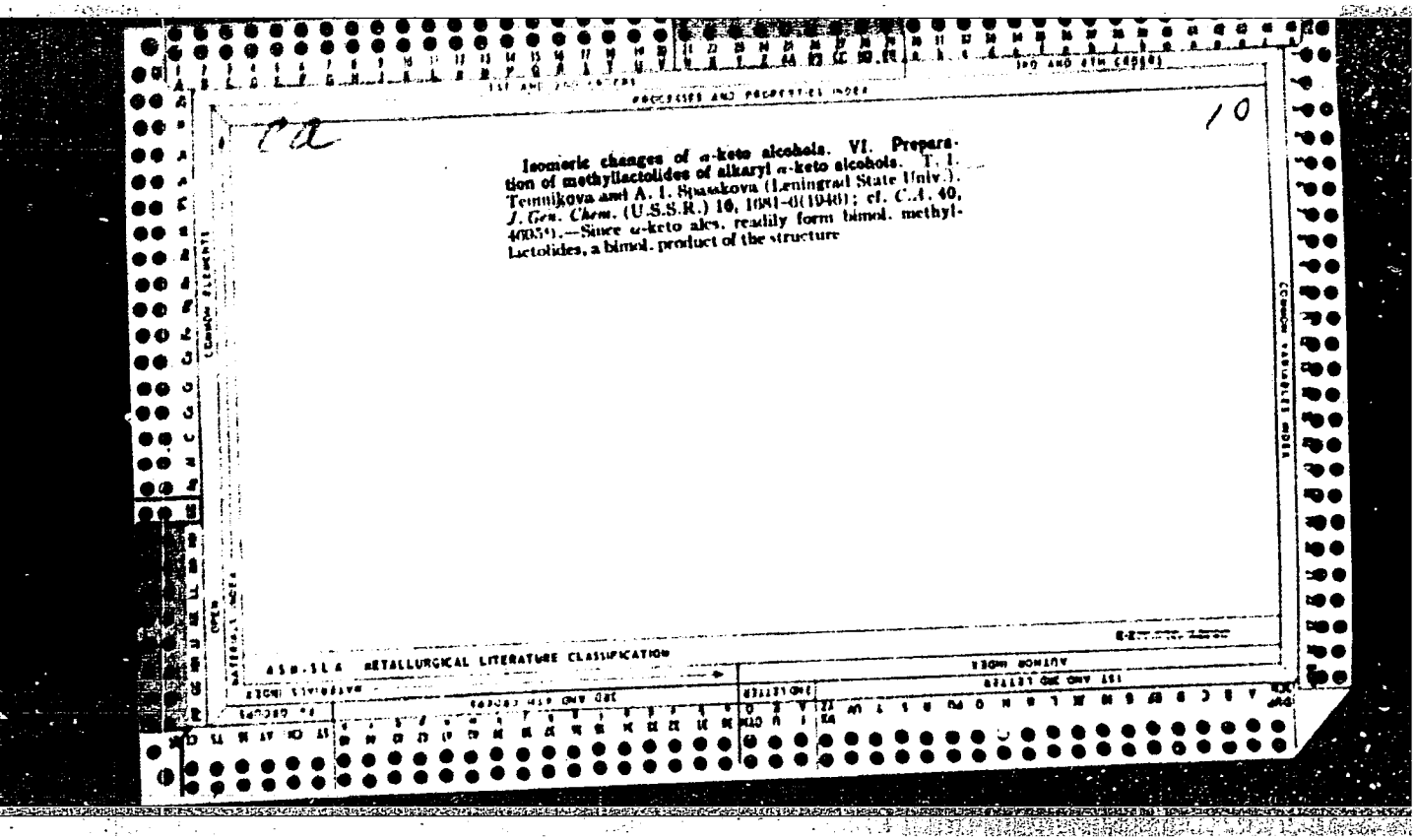
α-Keto oxides. I. Hydrogenation of aliphatic-aromatic α-keto oxides. T. I. Temnikova and V. F. Martynov (Leningrad State Univ.). *J. Gen. Chem.* (U.S.S.R.) 15, 499-513(1945)(English summary).—Chloroacetone (70 g.), 100 g. BzH, and 100 cc. MeOH were treated with cooling and stirring with MeONa (from 15 g. Na) in 230 g. MeOH; after filtration, treatment with water acidified by AcOH, and extn. with Et_2O there was obtained 80% *benzylideneacetone oxide* (I), b_{10} 134-7°, m. 58-7° (from MeOH, then petr. ether); *semicarbazone*, m. 140-1° (from EtOH). $ClCH_2COBz$ (30 g.) and 35 g. BzH in 10 cc. MeOH, treated as above with MeONa (from 6.3 g. Na) in 80 cc. MeOH, gave 54% *1-phenyl-2-propionylethylene oxide* (II), b_5 138-40°, m. 52-3° (from petr. ether); *semicarbazone*, m. 127-9° (from EtOH). Similarly, $MeCOCHClMe$ gave 61% *1-phenyl-2-acetylpropylene oxide*, b_5 113-14°, d_4^{20} 1.092, d_4^{15} 1.083, n_D^{15} 1.52186 (III); *semicarbazone*, m. 115-18° (from EtOH). Hydrogenation of these in Et_2O in the presence of Pt black was shown to proceed in steps with addn. of the 1st H_2 being 4-5 times faster than the addn. of the 2nd H_2; the addn. of H_2 to I and II gave oxides of the corresponding unsatd. alcs., while addn. of $2H_2$ gave the corresponding glycols. The products thus isolated were: *methylstyrylcarbinol oxide*, b_5 128-30°, d_4^{20} 1.105, n_D^{20} 1.53233, which, on treatment with water, in the presence of a several drops H_2SO_4, hydrated to *α-phenyl-γ-ethylglycerol*, m. 95-7° (from Et_2O); *ethylstyrylcarbinol oxide*, b_5 132-4°, m. 43-5° (from petr. ether), hydrated to *α-phenyl-γ-ethylglycerol*, m. 82-4° (from Et_2O); and *methylbenzylacetylcarbinol* (from III), b_5 118-19°, d_4^{20} 1.0605, d_4^{15} 1.0722, n_D^{20} 1.51258 (*semicarbazone*, 158-9° (from EtOH)), which failed to hydrate under the conditions given above. The glycols from the addn. of $2H_2$ were: *1-methyl-2-benzylethylene glycol*, m. 93-52-3°, b_{10} 154-5°; *1-ethyl-2-benzylethylene glycol*, b_5 109-3°-4°; and *1,2-dimethyl-1-benzylethylene glycol*, b_5 103-5°.

G. M. Kosolapoff

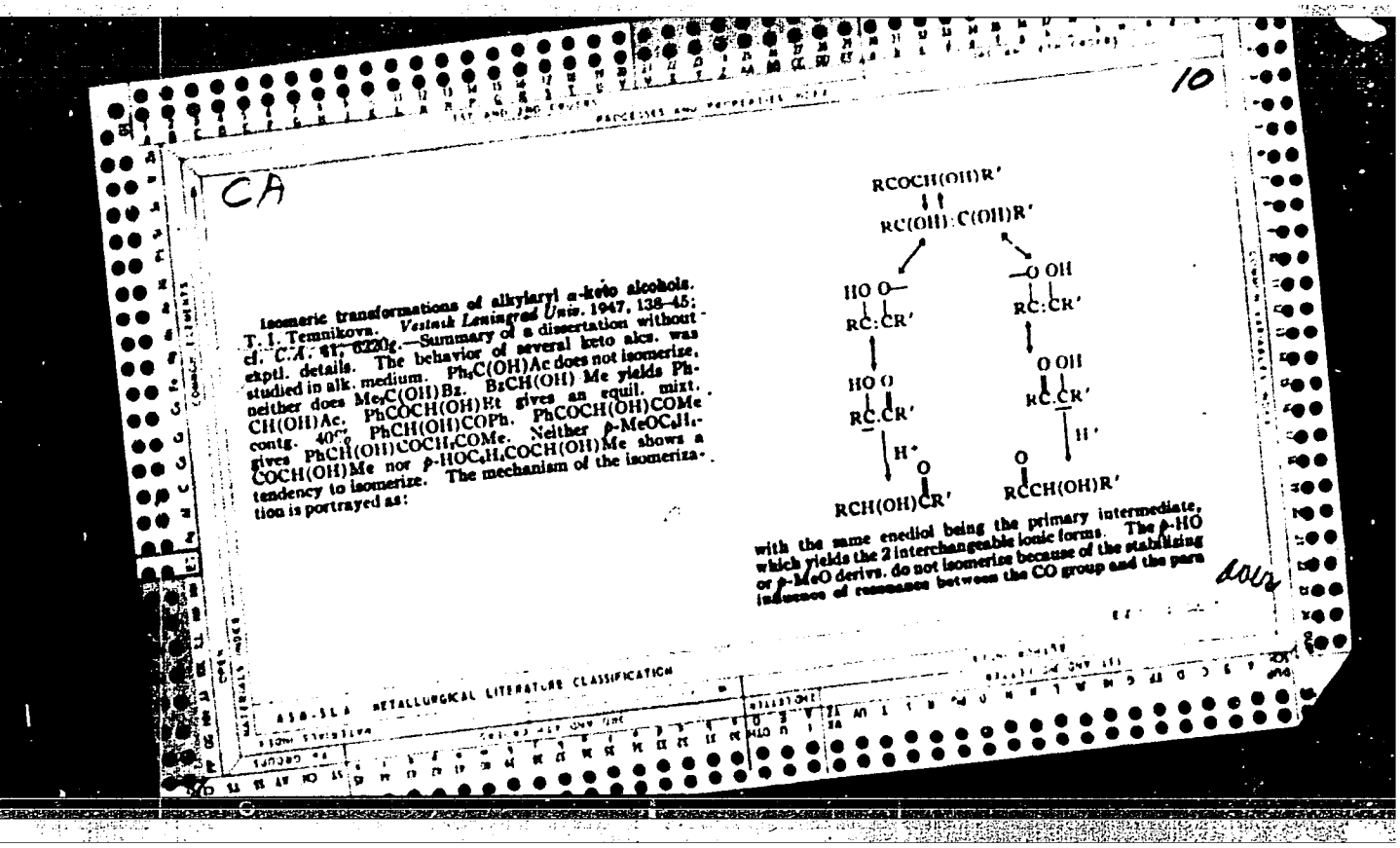
TEMNIKOVA, T. I.

"Investigation in the field of Isomeric Transformations of a-Keto-alcohols. V. Diphenyl-Acetyl-Carbinol and Dimethyl-Benzoyl-Carbinol." Temnikova, T. I. (p. 514)

SO: Journal of General Chemistry (Zhurnal Obshchei Khimii) 1945, Volume 15, no. 6.



Isomeric changes of α-keto alcohols. VI. Preparation of methyllactolides of alkaryl α-keto alcohols. T. I. Temnikova and A. I. Spasskova (Leningrad State Univ.). *J. Gen. Chem.* (U.S.S.R.) 10, 1081–6(1940); cf. *C.A.* 40, 4035⁵.—Since α-keto alcs. readily form bimol. methyllactolides, a bimol. product of the structure



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Isomeric transformations of alkylaryl α-keto alcohols. T. I. Temnikova. *Vestnik Leningrad Univ.* 1947, 138–45; cf. *C.A.* **41**, 6220g.—Summary of a dissertation without exptl. details. The behavior of several keto alcs. was studied in alk. medium. $Ph_2C(OH)Ac$ does not isomerize, neither does $Me_2C(OH)Bz$. BzCH(OH)Me yields PhCH(OH)Ac; PhCOCH(OH)Et gives an equil. mixt. contg. 40% PhCH(OH)COPh. PhCOCH(OH)COMe gives $PhCH(OH)COCH_2COMe$. Neither p-$MeOC_6H_4$COCH(OH)Me nor p-$HOC_6H_4COCH(OH)Me$ shows a tendency to isomerize. The mechanism of the isomerization is portrayed as:

with the same enediol being the primary intermediate, which yields the 2 interchangeable ionic forms. The p-HO or p-MeO derivs. do not isomerize because of the stabilizing influence of resonance between the CO group and the para

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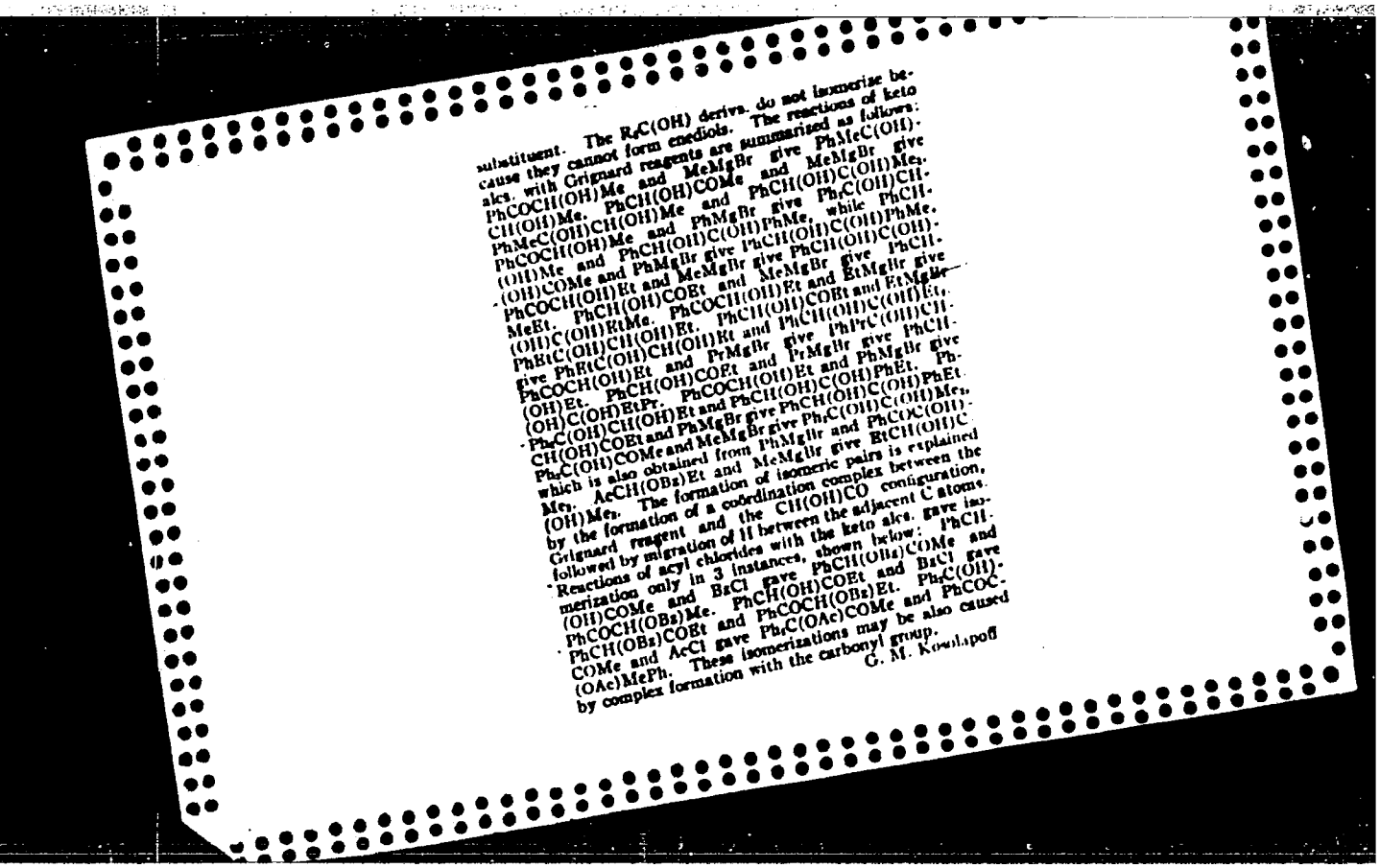

substituent. The $R_2C(OH)$ derivs. do not isomerize because they cannot form enediols. The reactions of keto alcs. with Grignard reagents are summarized as follows: PhCOCH(OH)Me and MeMgBr give PhMeC(OH)CH(OH)Me. PhCH(OH)COMe and MeMgBr give PhMeC(OH)CH(OH)Me and PhMgBr give PhC(OH)CH(OH)Me and PhCH(OH)C(OH)PhMe. PhCOCH(OH)Me and PhMgBr give PhC(OH)CH(OH)COMe and PhCH(OH)C(OH)Et and MeMgBr give PhCH(OH)C(OH)MeEt. PhCH(OH)COEt and MeMgBr give PhCH(OH)C(OH)EtMe. PhCOCH(OH)Et and EtMgBr give PhEtC(OH)CH(OH)Et. PhCH(OH)COEt and EtMgBr give PhEtC(OH)CH(OH)Et and PhCH(OH)C(OH)Et2. PhCOCH(OH)Et and PrMgBr give PhPrC(OH)CH(OH)Et. PhCH(OH)COEt and PrMgBr give PhPrC(OH)CH(OH)Et. PhCOCH(OH)Et and PhMgBr give PhCH(OH)C(OH)EtPr. PhCOCH(OH)Et and PhCH(OH)C(OH)PhEt. Ph2C(OH)CH(OH)Et and PhMgBr give PhCH(OH)C(OH)Me2. Ph2C(OH)COEt and MeMgBr give Ph2C(OH)C(OH)PhMe, which is also obtained from PhMgBr and PhCOC(OH)Me2. AcCH(OBz)Et and MeMgBr give EtCH(OH)C(OH)Me2. The formation of isomeric pairs is explained by the formation of a coördination complex between the Grignard reagent and the CH(OH)CO configuration, followed by migration of H between the adjacent C atoms. Reactions of acyl chlorides with the keto alcs. gave isomerization only in 3 instances, shown below: PhCH(OH)COMe and BzCl gave PhCH(OBz)C(O)Me and PhCOCH(OBz)Me. PhCH(OH)COEt and PhCOCH(OBz)Et. Ph2C(OH)CH(OBz)COEt and AcCl gave Ph2C(OAc)COMe and PhCOCH(OAc)MePh. These isomerizations may be also caused by complex formation with the carbonyl group.

G. M. Kosolapoff

PA 8/49T44

USSR/Chemistry - Ketones
Chemistry - Hydrogenation

Apr 48

"Studies in the Field of α-Keto-oxides: II, Obtaining of and Hydration of Oxides of Tri-Butyl-Styryl-Ketone," T. I. Temnikova, V. A. Kropachev, Chair of Constr of Org Compounds, Leningrad Order of Lenin State U, 7½ pp

"Zhur Obshch Khim" Vol XVIII (LXXX), No 4

The cis-and trans- forms of this oxide with melting point 70 - 71 and 80 - 81°, respectively, were obtained as two different isomers: $C_6H_5CHO + (CH_3)_3CCOCH_2Br +$ $CH_3ONa \rightarrow C_6H_5CH\text{-}CHOCOC(CH_3)_3 + NaBr + CH_3OH$. In both cases phenyl trimethylacetyl ethylene glycol

8/49T44

USSR/Chemistry - Ketones (Contd)

Apr 48

was obtained by hydration with sulfuric acid. The oxide could not be hydrogenated in the presence of platinum black, but in the presence of nickel, benzyl trimethyl acetyl carbinol was obtained. Submitted 24 Mar 1947.

8/49T44

CA

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Research in the field of cyclic acetals of hydroxycarbonyl compounds. I. Synthesis and properties of the methyl lactolide of methylbenzoylcarbinol (1-methoxy-1-phenyl-1-propene oxide). T. I. Temnikova and E. N. Kropacheva (Leningrad State Univ.). *J. Gen. Chem.* (U.S.S.R.) 19, No. 10, 1853–93(1949)(English translation).—See *C.A.* 44, 1929b.
E. J. C.

PROCESSES AND PROPERTIES INDEX

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α-Ketonic ethers. III. Selectivity of hydrogenation of benzalacetone ether (oxide) in the presence of platinum and palladium. T. I. Temnikova and V. A. Kropachev (J. gen. Chem. USSR, 1949, 19, 841—851 [U.S. transl.]).—Hydrogenation of 1 : 2-epoxy-1-phenylbutan-3-one (benzalacetone oxide) over Pt gives 1 : 2-epoxy-1-phenylbutan-3-ol; with Pd the product is [illegible]-1-phenylbutan-3-ol [illegible] $CH_2Ph \cdot CHAc \cdot OH$. The general rule is formulated that in the hydrogenation of oxides derived from aliphatic-aromatic unsaturated alcohols or ketones, the oxide ring is ruptured at the [illegible] group. Addition reactions of alcohols to epoxides are [illegible] and classified (no examples given.)

Reduction of 1 : 2-epoxy-1-phenylbutan-3-one (I) with H_2 over Pd black at [illegible] affords 1-phenylbutan-2-ol-3-one, $C_{10}H_{12}O_2$ ([illegible]%), b.p. 98°/1 mm., d^{20} 1·0883, n^{20} 1·5[illegible] (semicarbazone, $C_{11}H_{15}O_2N_3$, m.p. 169—170°; phenylosazone, $C_{22}H_{22}N_4$, m.p. 171—172°), which reacted with PhMgBr in Et_2O yields 1 : 3-diphenylbutane-2 : 3-diol, $C_{16}H_{18}O_2$, m.p. 108·5—109·5°. Oxidation of the latter [illegible] with CrO_3-$KHSO_4$-H_2O gives COPhMe and BzOH. Reduction of (I) with H_2 over Pt black or Pt-Ni leads to 1 : 2-epoxy-1-phenylbutan-3-ol (not isolated).

M. DAVIS.

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

USSR/Chemistry - Ketones, Bromo-
Reactions, Anomalous Jul 49

"The Anomalous Reactions of Alpha-Bromoketones: III, Research on Alpha-Bromo-n-Tolylacetone (I)," T. I. Temnikova, V. I. Vekšler, Chair of Structure of Org Compounds, Leningrad Ord of Lenin State U imeni A. A. Zhdanov, 6 pp

"Zhur Obshch Khim" Vol XIX, No 7

Chief product of reaction of I with potassium acetate was shown to be acetic ester of n-tolylacetylcarbinol, with only a small part of reaction accompanied by molecular rearrangement with formation of isomeric

2/50754

USSR/Chemistry - Ketones, Bromo-
Reactions, Anomalous (Contd) Jul 49

ester from methyl-n-tolyl-carbinol. Comparison of these results with those of reaction of potassium acetate with alpha-bromophenylacetone revealed that increased electron density in reactive zone results in a marked increase in reaction zone results in its interaction with potassium acetate, and a greatly decreased quantity of anomalous product of reaction. Submitted 16 Feb 48

2/50754

CA

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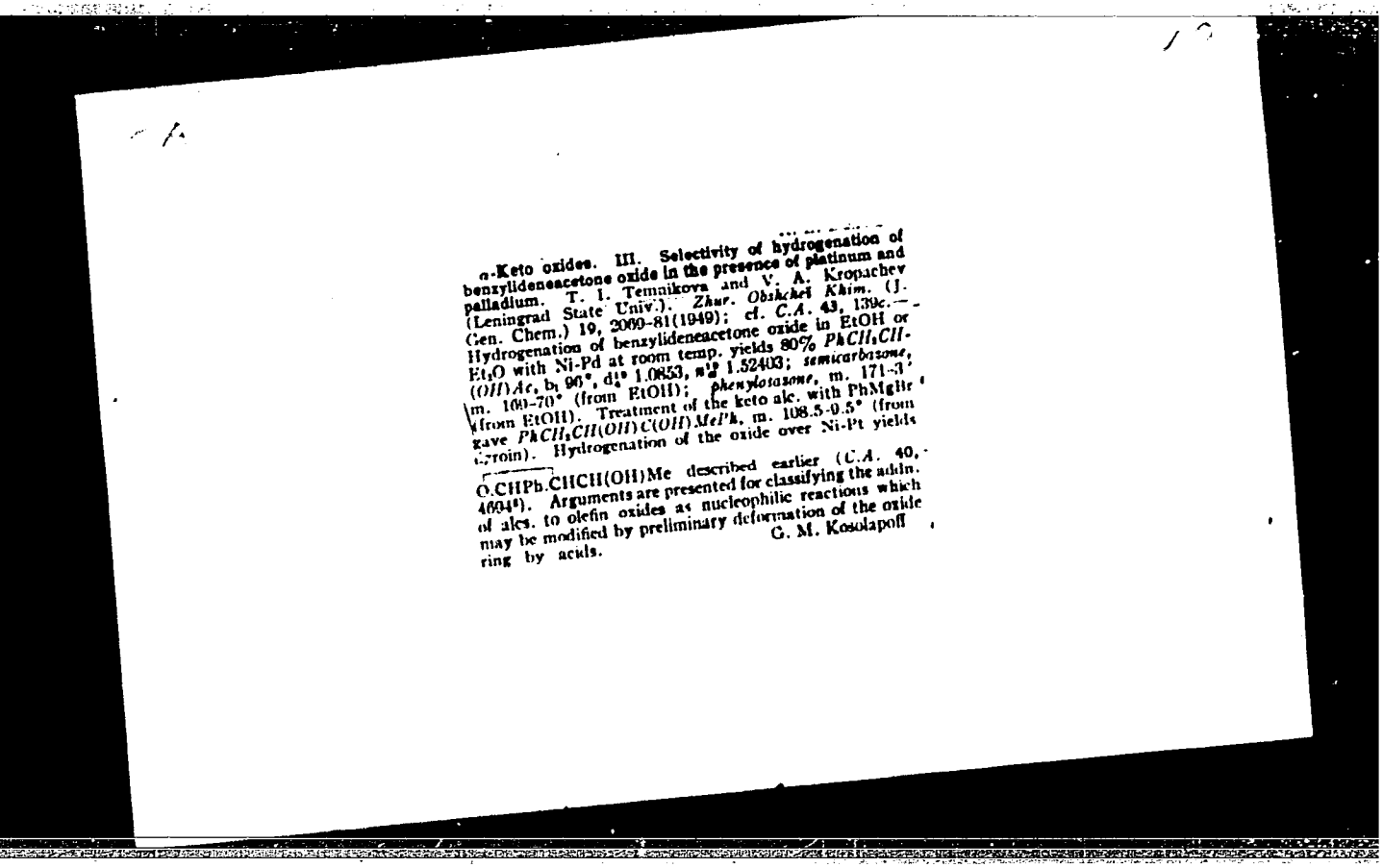
Isomeric transformations of α-keto alcohols. VII. Influence of chlorine in the para position on the stability of alkaryl α-keto alcohols. Methyl(p-chlorobenzoyl)-carbinol. T. I. Temnikova and E. I. Kulachkova. *Zhur. Obshchei Khim.* (J. Gen. Chem.) 19, 1324-34 (1949); cf. *C.A.* 41, 6239*f*.—Slow addn. of 50 g. PhCl and 50 g. EtCOCl to 116 g. $AlCl_3$ in 100 ml. CS_2 and letting stand 2 days, followed by 3 hrs. on a steam bath, gave upon ice treatment 91%, *Et p-chlorophenyl ketone*, m. 34-6°. This (61.2 g.) in 180 ml. AcOH, treated with 58 g. Br and poured into water, gave 80-90% *1-bromoethyl p-chlorophenyl ketone*, m. 77-9° (from ligroin). Heating this (13 g.) with 10 g. KO_2CH and 35 ml. MeOH in a sealed tube 8 hrs. at 128-30° gave 4.3 g. mixed *p-ClC₆H₄COCH(OH)Me* and *p-ClC₆H₄CH(OH)COMe*, $b_{0.4}$ 138-9°, which gave a *semicarbazone*, m. 183-4° (from EtOH); however, the presence of 2 products is shown by treatment with PhMgBr which gave a glycol mixt., m. 74-81° (from ligroin), apparently *p-ClC₆H₄C(OH)PhCH(OH)Me* (I) and *p-ClC₆H₄CH(OH)C(OH)PhMe*, since oxidation by $Pb(OAc)_4$ in AcOH gave *p*-ClC_6H_4COPh, PhAc, AcH, and *p*-$ClC_6H_4CO_2H$. Heating the crude oil from the KO_2CH-MeOH reaction 30 hrs. with an aq. suspension of $BaCO_3$ on a steam bath causes isomerization of the keto alc. mixt. to pure *methyl(p-chlorobenzoyl)carbinol* (46% yield), b_{16} 150-2°, $d_4^{21.4}$ 1.2365, $n_D^{21.6}$ 1.54738, which yields a *semicarbazone*, m. 186-8°, while reaction with PhMgBr yields pure I, m. 88.5-9.5°, which with $Pb(OAc)_4$ gives only *p*-ClC_6H_4COPh and AcH. A similar isomerization, with poorer yield, takes place on standing 3 days in 1.7% alc. KOH. Refluxing 25 g. *p*-$ClC_6H_4COCHBrMe$ with 12 g. KOAc and 50 ml. EtOH 5 hrs. gave 48.5% *methyl(p-chlorobenzoyl)carbinol acetate*, b_1 133-6° d_4^{20} 1.216, n_D^{20} 1.5230, which on treatment with MeMgBr gave *p-ClC₆H₄C(OH)MeCH(OH)Me*, b. 125°, which with $Pb(OAc)_4$ gave AcH and *p*-ClC_6H_4COMe (semicarbazone, m. 192-4°, also prepd. by the Friedel-Crafts method). The use of BzOK instead of KOAc in the above gave the corresponding *benzoate*, m. 92-3.5° (from ligroin), which is stable to hot aq. $BaCO_3$ (30 hrs.). The results indicate that the mesomeric effect of the *p*-ClC_6H_4 group is greater than that of Me in the intermediate substance formed in the course of isomerization. G. M. Kolsolapoff

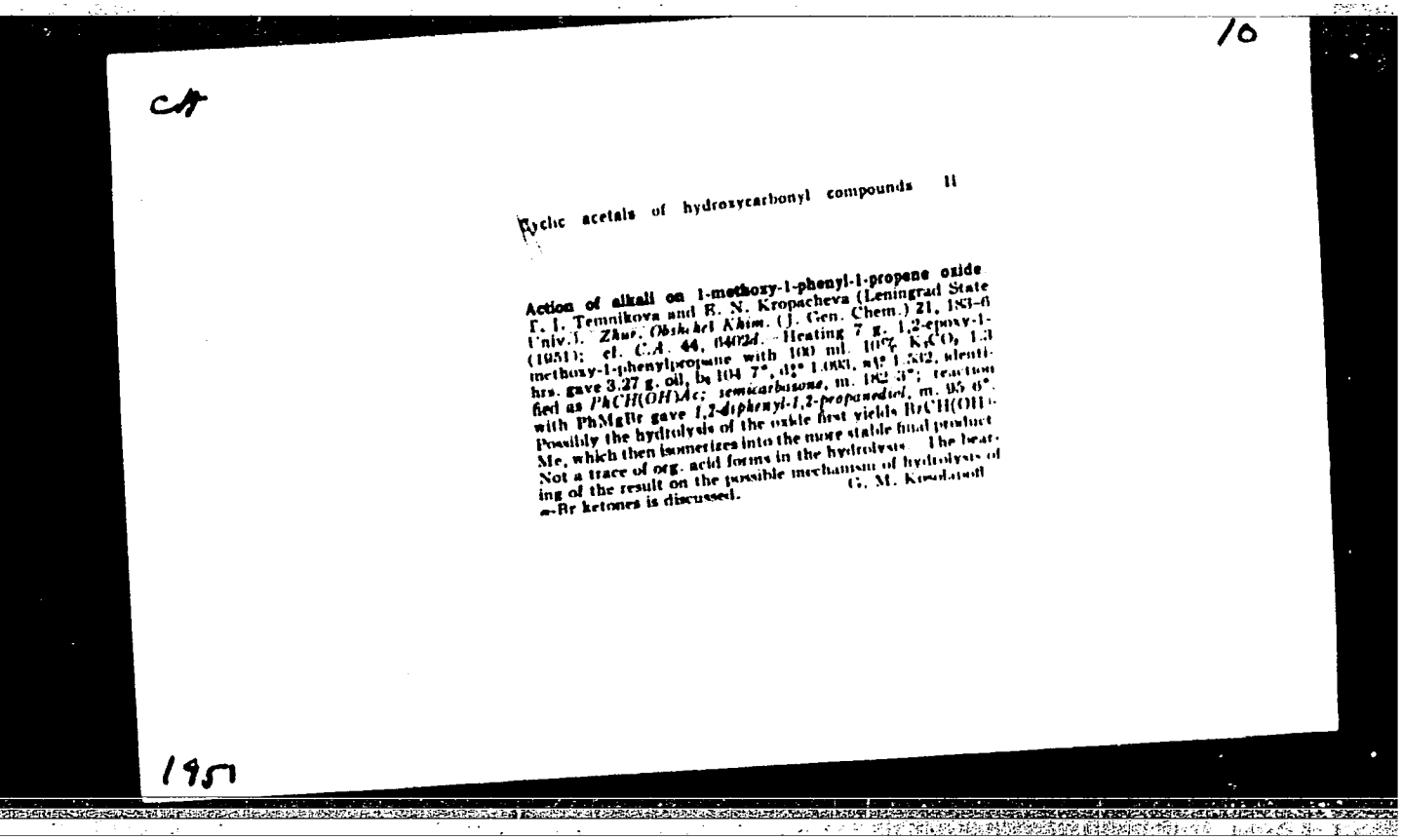
CA

Cyclic acetals of hydroxycarbonyl compounds. I. Preparation and properties of the methyl lactolide of methylbenzoylcarbinol (1-methoxy-1-phenyl-1-propene oxide). T. I. Temnikova and E. N. Kropacheva (Kafedra Stroeniya Org. Soedinenii Leningrad. Gosudarst. Ordena Lenina Univ. im. A. A. Zhdanova). *Zhur. Obshchei Khim.* (J. Gen. Chem.) 19, 1917-20(1949).—PhCOCHBrMe (32 g.) in Et_2O treated slowly with a suspension of MeONa (from 10 g. Na) in Et_2O yielded 10 g. *1-methoxy-1-phenyl-1-propene oxide*, Ph(MeO)C.CHMe.O, b_6 63.5°, d_4^{20} 1.0521, n_D^{20} 1.49004, which polymerizes on standing (mol. wt. doubles in 24 hrs.). The product (0.5 g.) treated with 1.5 g. $PhNHNH_2$ in EtOH contg. a little AcOH, heated 0.5 hr. on a steam bath, and let stand overnight gave 0.45 g. *PhC(:NNHPh)CHMeNHNHPh*, m. 126° (from EtOH). Heating the oxide with H_2SO_4 in all dilns. gave mostly tars; with 5% H_2SO_4 there was obtained a very low yield of a solid, m. 208° ($C_{18}H_{20}O_4$), and phenylacetylcarbinol, b_{12} 120-1° (semicarbazone, m. 189°). Addn. of the oxide (8.5 g.) to 5% H_2SO_4 preheated to 80° and stirring 1.5 hrs. on a steam bath gave 3.43 g. methylbenzoylcarbinol, $b_{1.5}$ 83-5°, n_D^{20} 1.54571 (forms a semicarbazide, m. 230°, on prolonged standing with the reagent). Reaction of this hydrolysis product with PhMgBr gave *1,1-diphenyl-1,2-propanediol*, m. 91-2° (from petr. ether), which gives Ph_2CO on chromic acid oxidation. Addn. of 3 ml. 3% MeOH-HCl to 0.5 g. oxide gave, after vigorous action, 0.3 g. *2,5-dimethoxy-2,5-dimethyl-3,6-diphenyl-p-dioxane*, m. 251° (from C_6H_6). The nomenclature of olefin oxides and lactols is discussed; the use of the prefix cyclo for the ring forms is urged. C. M. Kosolapoff



α-Keto oxides. III. Selectivity of hydrogenation of benzylideneacetone oxide in the presence of platinum and palladium. T. I. Temnikova and V. A. Kropachev (Leningrad State Univ.). *Zhur. Obshchei Khim.* (J. Gen. Chem.) 19, 2099–81(1949); cf. *C.A.* 43, 139c.—Hydrogenation of benzylideneacetone oxide in EtOH or Et_2O with Ni-Pd at room temp. yields 80% *PhCH₂CH(OH)Ac*, b. 90°, d_4^{20} 1.0853, n_D^{20} 1.52403; *semicarbazone*, m. 169–70° (from EtOH); *phenylosazone*, m. 171–3° (from EtOH). Treatment of the keto alc. with PhMgBr gave *PhCH₂CH(OH)C(OH)MePh*, m. 108.5–9.5° (from benzoin). Hydrogenation of the oxide over Ni-Pt yields O.CHPh.CHCH(OH)Me described earlier (*C.A.* 40, 4694[8]). Arguments are presented for classifying the addn. of alcs. to olefin oxides as nucleophilic reactions which may be modified by preliminary deformation of the oxide ring by acids.

G. M. Kosolapoff



10

Cyclic acetals of hydroxycarbonyl compounds II

Action of alkali on 1-methoxy-1-phenyl-1-propene oxide. T. I. Temnikova and E. N. Kropacheva (Leningrad State Univ.). *Zhur. Obshchei Khim.* (J. Gen. Chem.) 21, 183–6 (1951); cf. *C.A.* 44, 6402*d*. Heating 7 g. 1,2-epoxy-1-methoxy-1-phenylpropane with 100 ml. 10% K_2CO_3 1.5 hrs. gave 3.27 g. oil, bp 104.7°, d_4^{20} 1.0881, n_D^{20} 1.502, identified as *PhCH(OH)Ac*; *semicarbazone*, m. 182.3°; reaction with PhMgBr gave *1,2-diphenyl-1,2-propanediol*, m. 95.6°. Possibly the hydrolysis of the oxide first yields $BrCH(OH)$-Me, which then isomerizes into the more stable final product. Not a trace of org. acid forms in the hydrolysate. The bearing of the result on the possible mechanism of hydrolysis of α-Br ketones is discussed. G. M. Kosolapoff

1951

CA 10

α-Keto oxides. IV. Hydrogenation of α-keto oxides as a method of preparation of α-keto alcohols. V. I. Lemnikova and V. A. Kropachev (A. A. Zhdanov State Univ., Leningrad). *Zhur. Obshchei Khim.* (J. Gen. Chem.) 21, 201-8(1951); cf. *C.A.* 44, 7271e. The previously proposed hydrogenation of α-keto oxides over Pd-Ni is a generally applicable method for addn. of 2 H, after which the reaction stops. Almost no addn. of H occurs with iso-Pr styryl ketone oxide over Pt black. Addn. of 14.5 g. iso-PrCOBr to CH_2N_2 in Et_2O, followed by passage of HBr at 0°, gave 74% *bromomethyl iso-Pr ketone*, b_{10} 84-6°, n_D^{20} 1.4678. This (15.7 g.) and 13 g. BzH in 10 ml. MeOH slowly treated at 5° with 2.15 g. Na in 50 ml. MeOH, stirred 1 hr., and treated with dil. AcOH, gave 65% *iso-Pr styryl ketone oxide*, $C_{12}H_{14}O_2$, b_6 116.5-17.5°, d_4^{20} 1.055, n_D^{20} 1.5180 (liberates iodine from AcOH-KI, does not yield CH_4 with MeMgI, reduces Fehling soln. only on boiling); *semicarbazone*, m. 77-80° (from MeOH), 137-40° (on rapid heating in sealed tube) (from EtOH). Hydrogenation over Pt black did not proceed at normal conditions. Hydrogenation over Pd-Ni catalyst (by reduction of $PdCl_2.2NaCl$ and Ni; cf. previous papers) gave the keto alc., *$PhCH_2CH(OH)CO.CHMe_2$*, b_4 125°, d_4^{20} 1.065, n_D^{20} 1.5106; *semicarbazone*, m. 136.5-7.5° (from dil. MeOH); neither the *p*-nitrophenylhydrazone nor osazone could be made. The keto alc. (1.95 g.) with MeMgBr readily gave 80% *2,3-dimethyl-5-phenyl-3,4-pentanediol*, needles, m. 101.5-2.5° (from petr. ether), which on oxidation with $Pb(OAc)_4$ gave iso-PrCOMe, and BzOH. Similar hydrogenation of Et styryl ketone oxide gave 78-84% *benzylpropionylcarbinol*, b_4 116-16.5°, d_4^{20} 1.0819, n_D^{20} 1.5165 [*semicarbazone*, m. 140-0.5° (from EtOH)], which with PhMgBr gave 76% *1,3-diphenyl-2,3-pentanediol*, m. 83.5-4.5°, yielding EtCOPh and BzOH with $Pb(OAc)_4$.

G. M. Kosolapoff

Chem A

10

Isomeric transformations of α-keto alcohols. VIII. Effect of a methyl group in the para position in a phenyl nucleus on the relative stability of isomeric alkaryl α-keto alcohols. T. I. Temnikova and L. A. Petrova (Leningrad State Univ.). *Zhur. Obshchei Khim.* (J. Gen. Chem.) 21, 677-86(1951); cf. C. A. 44, 1026d, 1112f. Introduction of Me into the para position of Ph in alkaryl α-keto alcs. changes the properties of the substances by the inductive and mesomeric effects of the Me group. Of $MeC_6H_4COCH(OH)Me$ and $MeC_6H_4CHOHCOMe$, the former is most stable. A satd. soln. of 30 g. HCO_2K in MeOH at 40° is treated with a 50% MeOH soln. of p-$MeC_6H_4CHBrAc$ (31 g. p-$MeC_6H_4CH_2Ac$ brominated and the crude product used directly) and stirred at gentle reflux 10 hrs. to yield 27% [illegible] (I), b_1 100-1°, $b_{1.5}$ 103-6°, which on standing rapidly deposits a solid residue; *semicarbazone*, m. 189-91° (from EtOH); *oxazone*, m. 141-3° (from EtOH). Treatment of the alc. with 2-3% MeOH-HCl yields the *cyclodimethylditolylide*, $C_{20}H_{20}O_4$, m. 258°. Attempts to prep. the carbinol by heating the Br ketone in a sealed tube with HCO_2K at 110° gave [illegible] isolated as the [illegible] sealed tube). The *solid* m. 155°, formed on storage of the carbinol, has no OH groups, nor does it form a semicarbazone; possibly it is (p-MeC_6H_4C [illegible]). Heating p-$MeC_6H_4COCHBrMe$ with HCO_2K and MeOH in a sealed tube [illegible] hrs. at 110° gave 37% product (II), b_1 120-31°, b_1 100-10 [illegible]; semicarbazone, m. 188-9°, does not depress the m.p. of I semicarbazone; the yield of the semicarbazone indicates that the condensation yields a mixt. of keto alcs. contg. some 20-30% I. Treatment of the crude II with $H_2NCONHNH_2$ in aq. MeOH, filtration of the [illegible] semicarbazone, acidification of the filtrate with 5% H_2SO_4, warming on a steam bath, and extg. with Et_2O gave [illegible] *toluylcarbinol cyclodimethyl*[illegible], m. 250° (from C_6H_6). Heating BzCl with crude II and $BaCO_3$ failed to yield a Bz deriv., but heating 4 g. p-$MeC_6H_4COCHBrMe$ and 1.2 g. BzOK in EtOH readily gave *methyl*[illegible] *benzoate*, m. 96-9° (from ligroin). The isomerization of the 2 keto alcs. was followed by thermal analysis of their lactolides. Crude II on this basis contains 20-5% I and 75-80% p-$MeC_6H_4COCH_2OH$ Me (III). Heating this mixt. (6.4 g.) 20 hrs. to 100° with fresh $BaCO_3$ in a CO_2 stream gave the cyclolactolide, m. 258°, corresponding to 90-5% III. Heating substantially pure I under similar conditions gave a cyclolactolide whose m.p. [illegible] 23.8% III concn. The cyclolactolide [illegible] The pure [illegible] m.p. at about 210°, at approx. 50% I concn. [illegible] individual keto alcs. could not be isolated. G. M. K.

1951

USSR/Chemistry - Acetylene Derivatives Oct 51

"Action of Aluminum Amalgams on 3-Chloro-3-Methylbutyne-1," T. I. Temnikova, Z. A. Baskova, Chair of Structure of Org Compds, Leningrad State U imeni A. A. Zhdanov

"Zhur Obshch Khim" Vol XXI, No 10, pp 1823-1825

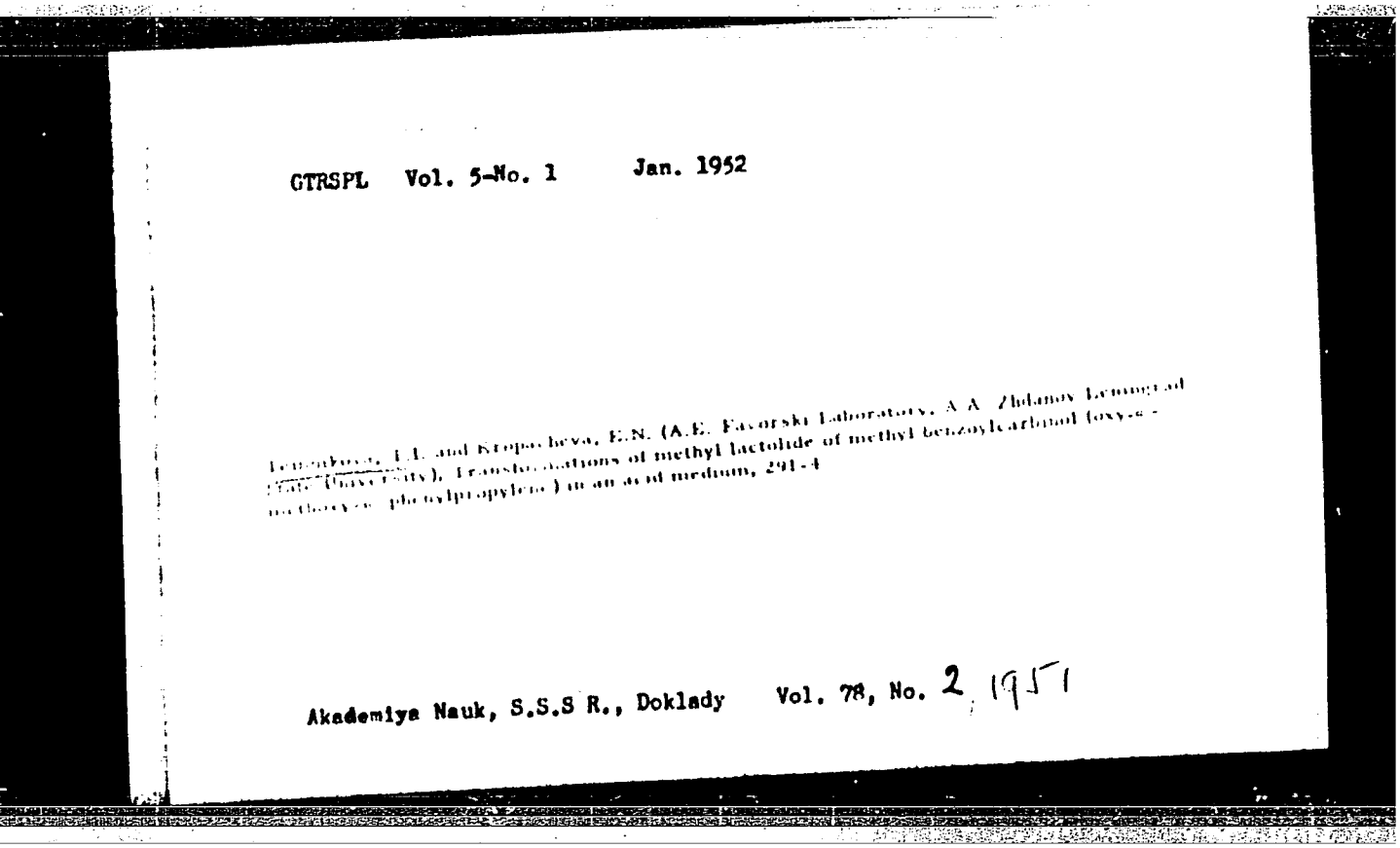
Reduction of 3-chloro-3-methylbutyne-1 with Al amalgam in boiling aq Et alc yields mixt of hydrocarbons: isopropylacetylene (~ 30%), isopropenylacetylene (~ 60%), and nonsym dimethylallene (~ 10%).

194T29

CA

10

Molecular rearrangements of α-keto alcohols. IX. Reaction of methyl *p*-tolyl ketols with organomagnesium compounds. T. I. Temnikova and L. A. Petrova (A. A. Zhdanov State Univ., Leningrad). *Zhur. Obshchei Khim.* (J. Gen. Chem.) 21, 1877–83 (1951); cf. *C.A.* 45, 9504h. Reactions of MeMgBr with *p*-$MeC_6H_4COCH(OH)Me$ (I) and *p*-$MeC_6H_4CH(OH)Ac$ (II) lead to considerable enolization of the latter substances. Introduction of a *p*-Me group thus enhances enolization and raises the yield of "abnormal" reaction products (*loc. cit.*). To MeMgBr (from 11.6 g. MeBr) in Et_2O was added 4.9 g. I with ice cooling and the mixt. let stand 12 hrs., refluxed 4 hrs., and worked up as usual, yielding 49.4% *p-MeC₆H₄CMe(OH)CH(OH)Me*, b_{16} 160–3°, m. 54–6°, which with CrO_3–H_2O at 50° gave AcH and *p*-AcC_6H_4Me. I (5 g.) with PhMgBr (from 19 g. PhBr) similarly gave 20% *1-phenyl-1-p-tolyl-1,2-propanediol*, m. 84–6°, which with $Pb(OAc)_4$–AcOH gave AcH and *p*-BzC_6H_4Me-*p*. II (5 g.) with EtMgBr yielded 1.7 g. oily product, b_4 143–9°, oxidized to AcH, MeEtCO, *p*-MeC_6H_4COEt, and *p*-$MeC_6H_4CO_2H$, thus showing that a mixt. of glycols formed; about 33% *3-p-tolyl-2,3-pentanediol* and 67% *1-p-tolyl-2-methyl-1,2-butanediol*. Similarly II with PhMgBr gave a mixt. of *glycols*, m. 87–8°, oxidized to AcH, *p*-BzC_6H_4Me, AcPh, and *p*-$MeC_6H_4CO_2H$, from the relative amts. of which the glycol mixt. was shown to be 85% *1-p-tolyl-2-phenyl-1,2-propanediol* and 15% *1-phenyl-1-p-tolyl-1,2-propanediol*. The reaction proceeds by a 1st step reaction of RMgX with the OH of the carbinol, followed by development of the pos. pole at the carbonyl C with addn. of MgBr to carbonyl the O, the subsequent course being detd. by the structure of the carbinol. G. M. Kosolapoff



GTRSPL Vol. 5-No. 1 Jan. 1952

Tsukervanik, I.P. and Kropacheva, E.N. (A.E. Favorski Laboratory, A.A. Zhdanov Leningrad State University). Transformations of methyl lactolide of methyl benzoylcarbinol (oxy-s-methoxy-s-phenylpropylene) in an acid medium, 291-4

Akademiya Nauk, S.S.S R., Doklady Vol. 78, No. 2, 1951

GTRSPL No. 45

Lemtakova, L.I. and Tikhomolova, M.P. (A.A. Zhdanov Leningrad State University). The structure of Butlerov's oxooctenol $(CH_3)_3C-C(OH)(CH_3)_2$, 613-6

Akademiya Nauk S.S.S.R., Doklady Vol. 79 No. 4, 1951

1. TEMNIKOVA, T. I.

2. USSR (600)

4. Chemistry, Organic

7. Molecular rearrangement, tautomeric and isomeric conversion. Part 1. Development of principle ideas in the works of A. M. Butlerov, Vest. Len. Un., 7, No. 2, 1952 .

9. Monthly List of Russian Accessions, Library of Congress, February 1953. Unclassified.

TEMNIKOVA, T. I.

Temnikova, T. I., Kropachev, V. A.- "Investigation of isomeric transformations of -keto alcohols. IX. Investigation of benzylacetylcarbinol." (p. 813)

SO: Journal of General Chemistry, (Zhurnal Obshchei Khimii), 1952, Vol. 22, No. 5

TEMNIKOVA, T.I.

Chemical Abst.
Vol. 48 No. 5
Mar. 10, 1954
Organic Chemistry

Isomeric transformations of α-oxo alcohols. X. Benzylacetylcarbinol. T. I. Temnikova and V. A. Kropachev (A. A. Zhdanov State Univ., Leningrad). *J. Gen. Chem. U.S.S.R.* 22, 875-7(1952)(Engl. translation).—See *C.A.* 47, 3268e. H. L. H.

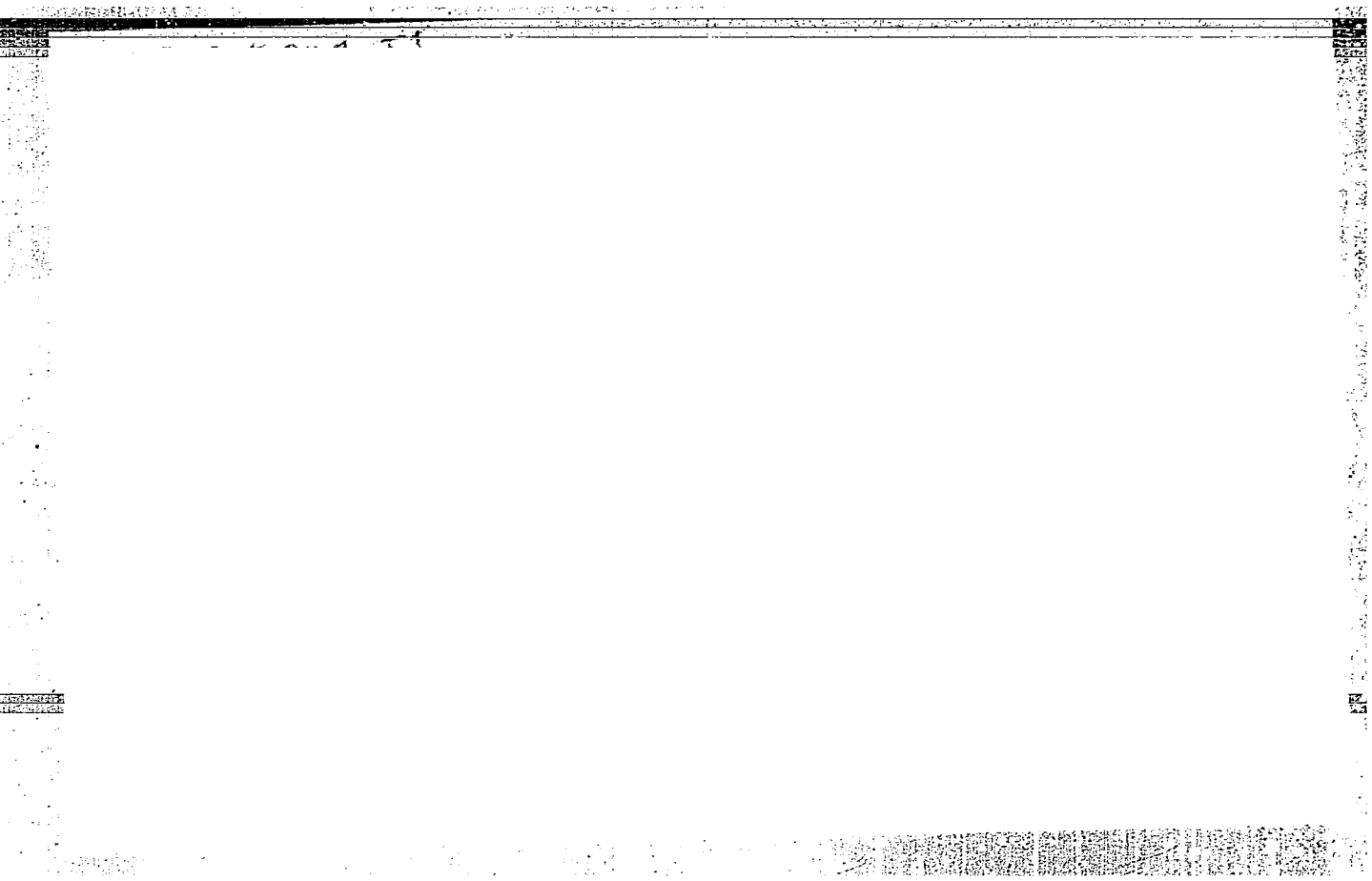
7-16-54

TERNIKOVA, T. I., KULACHKOVA-KITO, Ye. I.

Alcohols.

Molecular rearrangements of -keto alcohols. Part. II. Molecular rearrangements of esters of -keto alcohols during methanolysis. Zhur. ob.khim. 22 No. 3, 1952.

9. Monthly List of Russian Accessions, Library of Congress, November 1953, Uncl.



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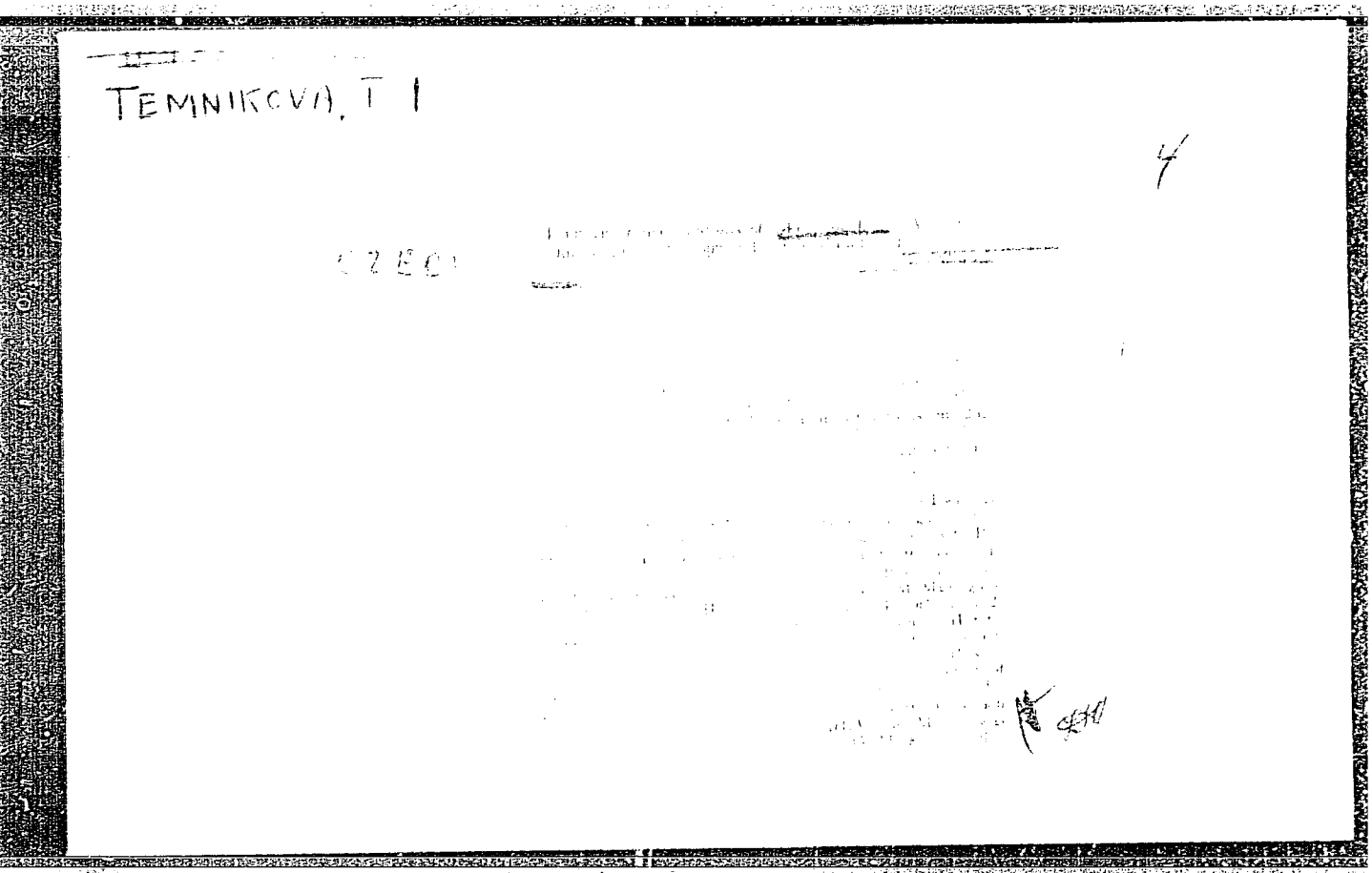
TEMNIKOVA, T. I.

(3)

Chemical Abst.
Vol. 48 No. 5
Mar. 10, 1954
Organic Chemistry

Molecular rearrangements of α-oxo alcohols. XI. Molecular rearrangements in methanolysis of esters of α-oxo alcohols. T. I. Temnikova and E. I. Kulachkova-Kmito (Zhdanov Leningrad State Univ.). *J. Gen. Chem. U.S.S.R.* 22, 1425-7(1952)(Engl. translation). See *C.A.* 47, 4857d. H. L. H.

MF 1-28-54



TEMNIKOVA, T. I., BASKOVA, Z. A. and KHAIMOVA, M. A.

On the Addition of Iodine Chloride to α,β-Diphenylpropylene and α,β-Diphenylethylene, page 874, Sbornik statey po obshchey khimii (Collection of Papers on General Chemistry), Vol II, Moscow-Leningrad, 1953, pages 1680-1686.

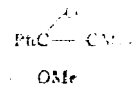
Chair of the Structure of Organic Compounds, Leningrad State U

"APPROVED FOR RELEASE: 07/16/2001 CIA-RDP86-00513R001755220014-4

Cyclic acetals of hydroxycarbonyl compounds. IV. Methyl lactolide of dimethylbenzoylcarbinol and its transformations. T. I. Temnikova and [illegible] (A. A. Zhdanov State Univ., Leningrad). *Zhur. Obshchei Khim.* 23, 1338-44(1953); cf. C.A. 48, 2654a. - To MeONa from 10 g. Na in 200 ml. Et_2O was added slowly 70 g. BzCBrMe$_2$ and after 7-10 hrs. the filtrate gave *dimethylbenzoylcarbinol Me lactolide*, PhC(OMe) CMe$_2$ O (I), b. 55-6.5°, b. 75-6.5°, d_{20} 1.0124, n_D^{20} 1.4979, [illegible] 1.49585, [illegible] 1.5093. I with aq. alc. $H_2NCONHNH_2$ AcOH gave dimethylbenzoylcarbinol semicarbazone, m. [illegible] I [illegible] g., with 2,4-$(O_2N)_2C_6H_3NHNH_2$ [illegible] aq. [illegible] with a trace of H_2SO_4 gave the [illegible] m. [illegible] gave BzC[illegible] Me$_2$ [illegible] CMe$_2$ [illegible] gave an oil which yielded [illegible] BzC(OH)Me$_2$ and a substance [illegible] possibly II [illegible] its absorption spectrum resembles that of the cyclic dimethyldimer [illegible] of BzCH [illegible] [illegible]

[illegible] the product is the same [illegible] [illegible] Me [illegible] Mg [illegible] Et$_2$O with 7 g. [illegible] and preheated until 2 layers formed; after 5 hrs. [illegible] yield of the isomeric [illegible] [illegible] whose semicarbazone [illegible] the ketone [illegible] max. of a CC group [illegible] no max. at 320 mμ. [illegible] oxidation

[illegible] NaOBr gave [illegible] V. Methyl lactolides of ethyl



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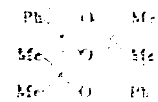

II

benzoylcarbinol and methyl p-anisoylcarbinol [illegible] To [illegible] g. MeONa suspended in [illegible] Et_2O [illegible] added [illegible] g. MeCHBrBz, the mixt. filtered after [illegible] hrs. at room temp. and the filtrate distd. giving [illegible] g. [illegible]

[illegible] which reacted [illegible] gave the [illegible] PhC(OMe)[illegible] Hydrolysis of [illegible] max. [illegible] The absorption max. [illegible] [illegible] Mg [illegible] Me [illegible]

[illegible] and unesterified [illegible]

[illegible] M. Kosolapoff

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TEMNIKOVA, T.I.; ALMASHI, N.I.

Investigation in the field of cyclic acetals of oxycarbonyl compounds. Part 5. Methyllactolides of ethylbenzoylcarbinol and methyl-*m*-anisoylcarbinol. Zhur.ob.khim. 23 no.9:1498-1500 S '53. (MLRA 6:10)

1. Laboratoriya im. A.Ye.Favorskogo. Leningradskiy Gosudarstvennyy universitet im. A.A.Zhdanova. (Lactolides)

USSR. CH (2)

Addition of iodine chloride to 1,1-diphenyl[illegible] and 1,1-diphenylethylene. T. I. Temnikova, Z. A. Baskova, [illegible] (Leningrad State Univ.). [illegible]

TEMNIKOVA, T.

USSR/Chemistry - Reaction processes

Card 1/1 Pub. 151 - 21/37

Authors : Temnikova, T., and Myukhyurdari, S.

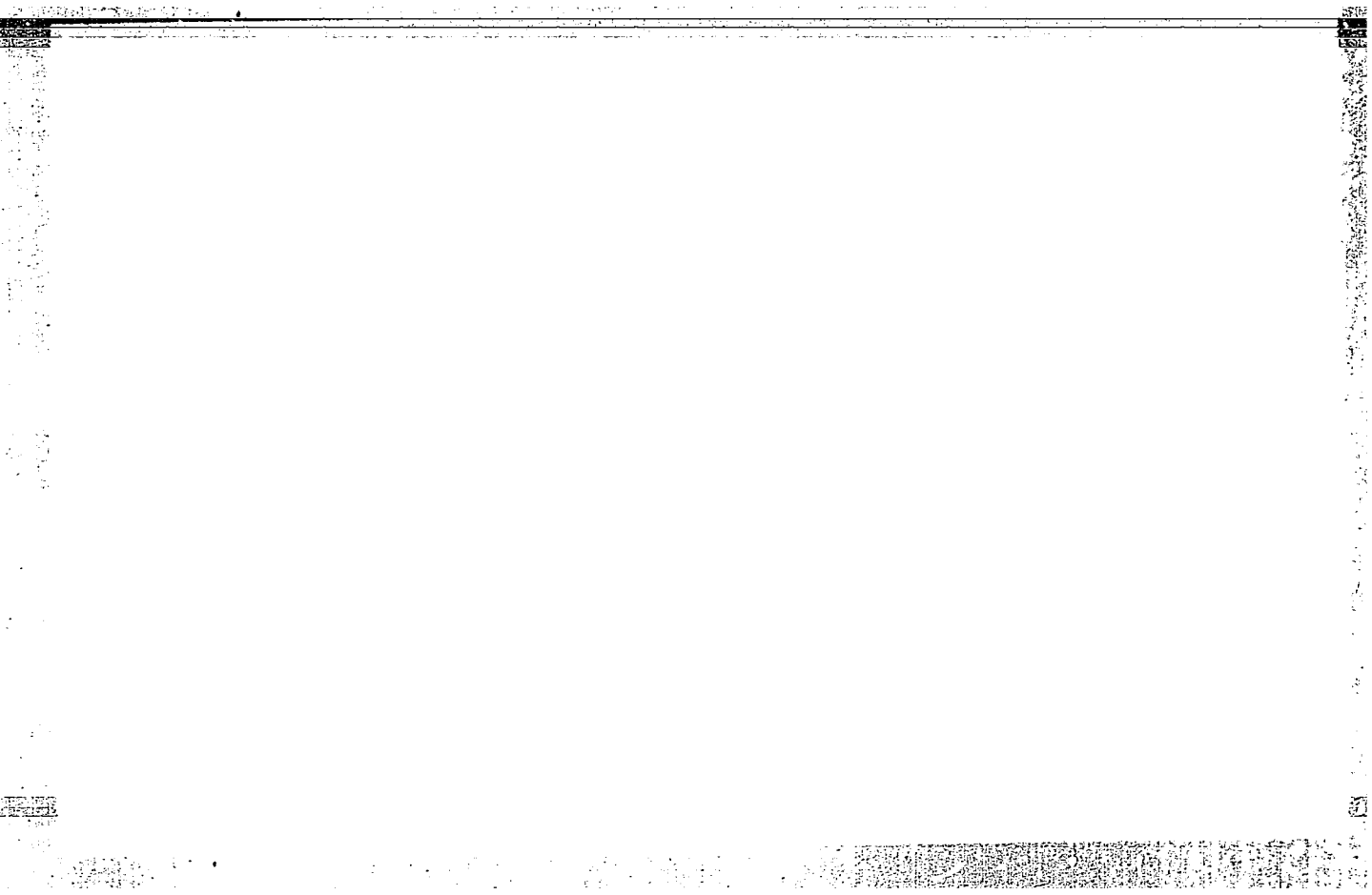
Title : About anomalous reactions of alpha-bromoketones. Part 4.- Reaction of sodium phenolate with alpha-bromoethylphenylketone.

Periodical : Zhur. ob. khim. 24/10, 1819-1823, Oct 1954

Abstract : The reaction between NaC_6H_5O and alpha-bromoethylphenylketone was investigated in anhydrous ether and in methyl alcohol. A direct relation between the solvent and the trend of the reaction was established. The products obtained from the reaction of the above mentioned compounds, in an ethyl ether medium and in methyl alcohol, are described. The products derived from the reaction between phenol and methyllactolite of methylbenzoylcarbinol are listed. Eight references: 5-USSR; 2-USA and 1-German (1906-1953).

Institution: State University, Leningrad

Submitted : February 20, 1954



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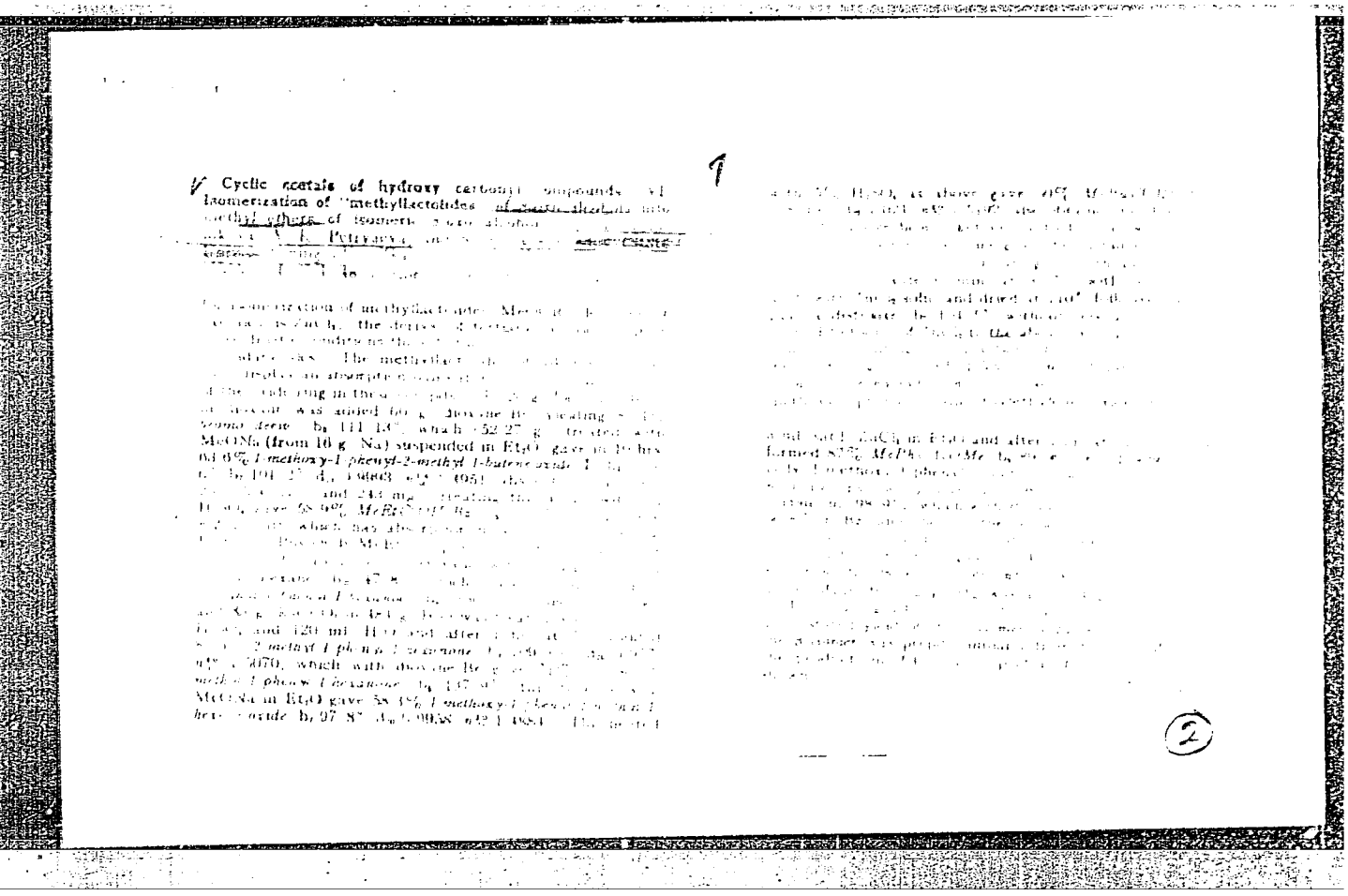

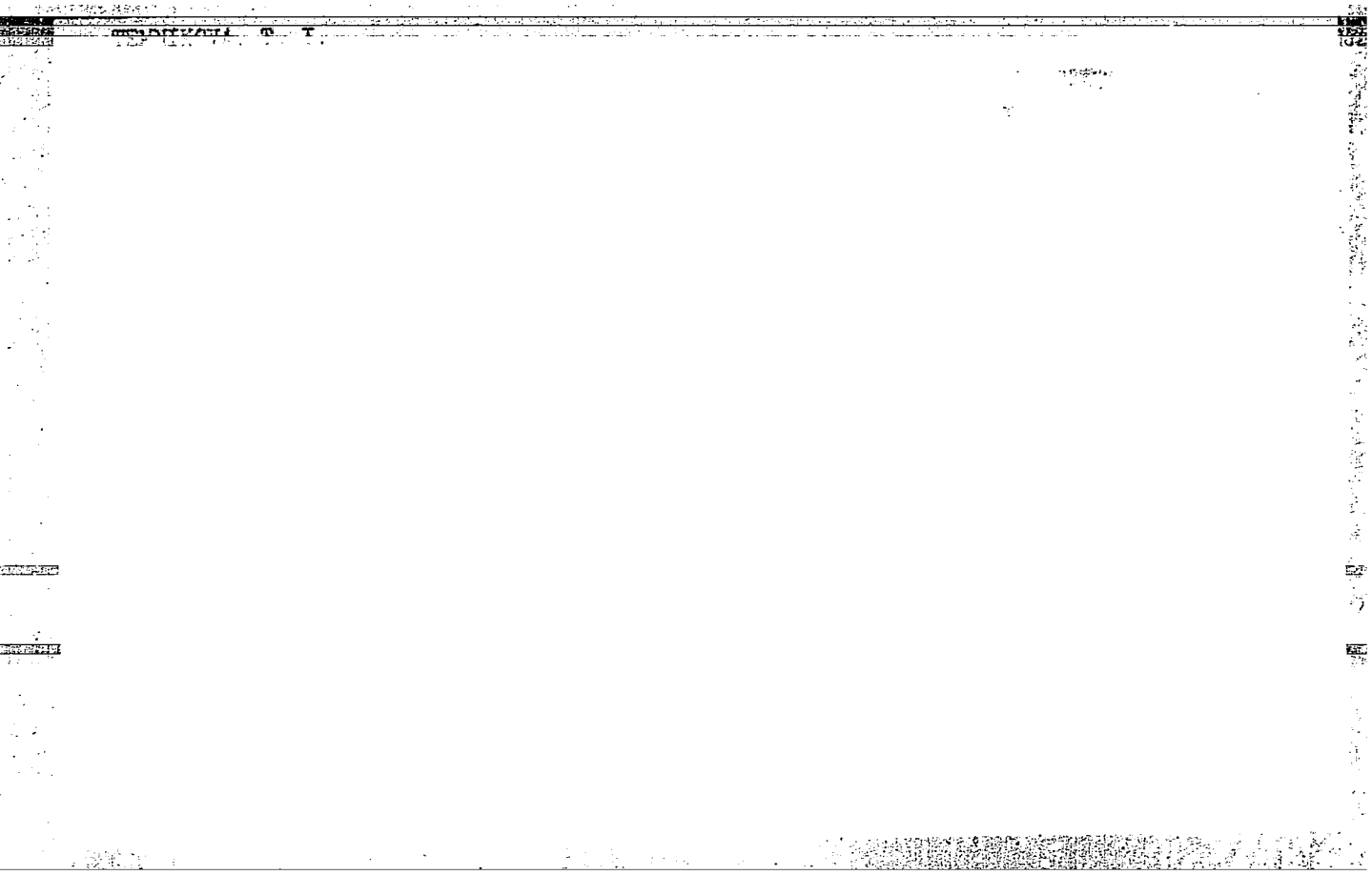

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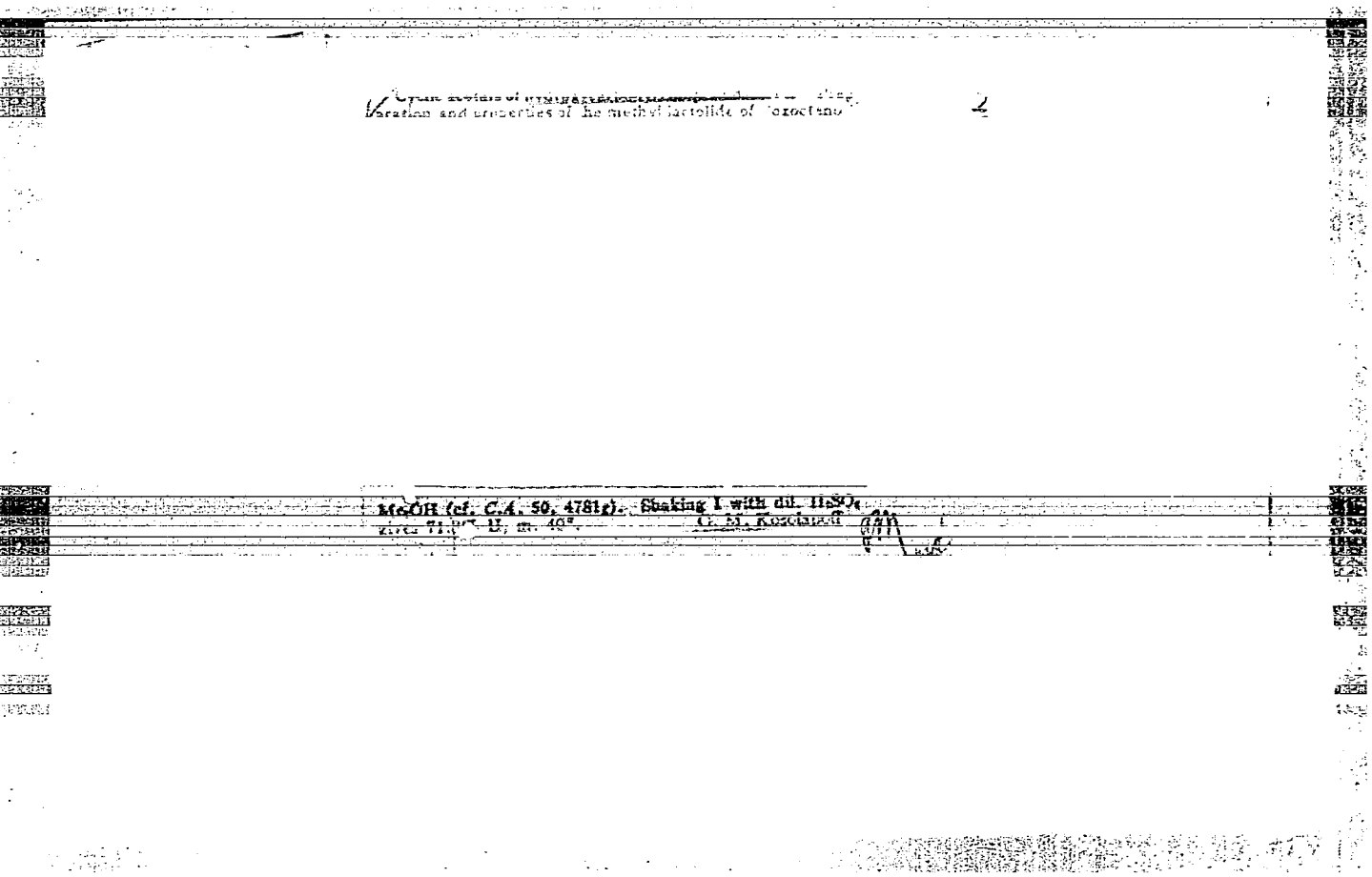

AUTHORS: Temnikova, T. I., and Ivanova, V. A. 79-2-14/58

TITLE: Investigation of Cyclic Acetals of Hydroxy Carbonyl Compounds. Part 8. Methyllactolide of Propylbenzoylcarbinol and its Conversions (Issledovaniye v oblasti tsiklicheskikh atsetaley oksikarbonil'nykh soyedineniy. VIII. Metillaktolid propilbenzoilkarbinola i yego prevrashcheniya).

PERIODICAL: Zhurnal Obshchey Khimii, 1957, vol 27, No 2, pp. 340-342 (U.S.S.R.)

ABSTRACT: The purpose of this experiment was to study the conversions of methyllactolides of alpha-ketoalcohols under the effect of acid reagents in the presence of carbohyl-containing substances and particularly in an acetone solution. The authors wanted to determine whether under such conditions the carbonyl-containing compound will attach itself to the oxide cycle and whether the conversion of the methyllactolide will be the same as in the presence of solvents inactive with respect to the addition reaction in the oxide cycle. The authors obtained and characterized methyllactolide of propylbenzoylcarbinol as an oxide of alpha-methoxy- alpha-phenyl-beta-propylethylene. Methyllactolide dimerizes easily into dioxane derivatives and hydrolyzes into keto-

Card 1/2

79-2-14/58

Investigation of Cyclic Acetals of Hydroxy Carbonyl Compounds. Part 8.

alcohol-propylbenzoylcarbinol.

Carbinol-containing substances could not be introduced into the reaction with methyllactolide of fatty-aromatic ketoalcohol. The reaction of anhydrous $SnCl_4$ with methyllactolide led to isomeric conversion of the latter into methyl ether of phenylpropylcarbinol.

There are 8 references, of which 5 are Slavic

ASSOCIATION: Leningrad State University

PRESENTED BY:

SUBMITTED: March 10, 1956

AVAILABLE: Library of Congress

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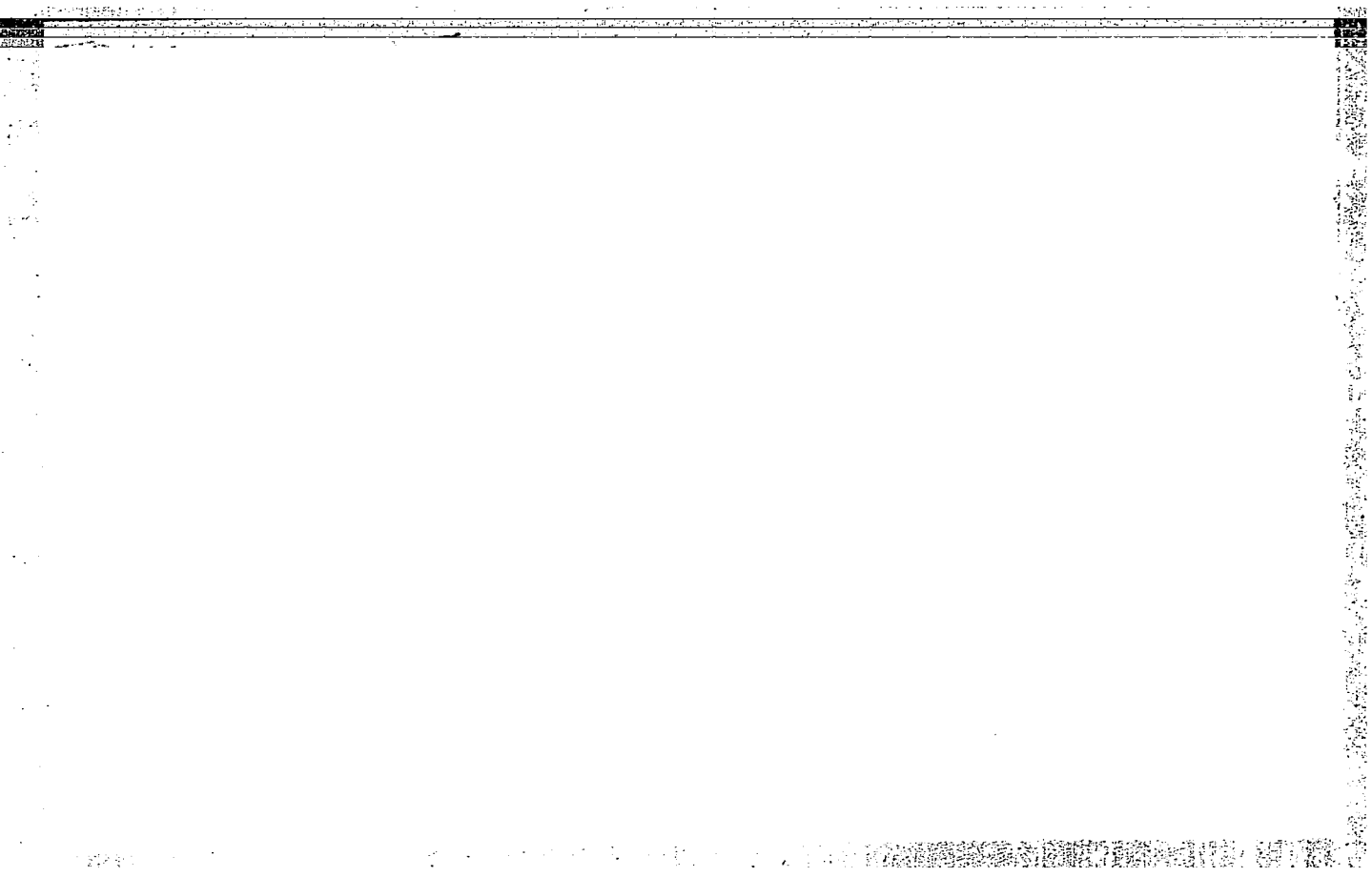

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TEMNIKOVA, T.I.; GONTAREV, B.A.

Benzylidene derivatives of the hydrate form of α-ketols containing 1,3-dioxolane cycles. Dokl. AN SSSR 112 no.3: 445-448 Ja '57. (MLRA 10:4)

1. Leningradskiy gosudarstvennyy universitet im. A.A. Zhdanova. Predstavleno akademikom I.N. Nazarovym.
(Ketols) (Toluene) (Dioxolane)

AUTHORS: Temnikova, T. I., Anikeyeva, A. N., Tikhomirova-Sidorova, N. S. SOV/79-28-12-2/41

TITLE: S. N. Danilov's Work in the Field of Isomeric Transformations and Molecular Regroupings of Carbonyl, Oxy-Carbonyl Compounds and Carbohydrates, and Their Theoretical Importance (Raboty S. N. Danilova v oblasti izomernykh prevrashcheniy i molekulyarnykh peregruppirovok karbonil'nykh, oksikarbonil'nykh soyedineniy i uglevodov i ikh teoreticheskoye znacheniye)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol 28, Nr 12, pp 3162-3173 (USSR)

ABSTRACT: Since Danilov's first work 45 years ago there has taken place a great change in theory concerning the problem of the molecular regroupings and isomeric transformations of oxygen-containing compounds; this was mainly due to Danilov's and his cooperators' work. At present it is taken for sure that molecular regroupings which complicate chemical processes in organic chemistry, depend kinetically on the displacement of the hydrogen atoms or the carbohydrate group into the adjacent position. The isomeric equilibrium transformations, which take place very easily in some cases under the influence

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of the catalysts favorable to these transformations, depend, like all equilibrium processes, on thermodynamic factors. According to detailed reports published by Danilov important conditions are mentioned that must be taken into consideration in interpreting the mechanism of molecular regroupings of the α-glycols. The basic idea throughout all his papers is that the process of transformation depends not only on the radicals but also on their interaction, on the dehydrating agent and on conditions under which the dehydration takes place. He and his cooperators systematically investigated the behavior of α-oxy-aldehydes under the action of various catalysts, which led to important results. The oxy-aldehyde-oxy-ketone regrouping in acid medium according to Danilov takes place under an intermediate formation of α-alcohol oxides (scheme on page 3167). The manifold types of isomeric transformations and molecular regroupings were illustrated by Danilov with supplementary informations offered by other scientists according to the scheme of transitions of genetically related

compounds as mentioned on page 3169 (upper half); this was carried out, for instance, in the case of compounds with two phenyl groups and two carbon atoms in the chain (the big arrows point to the transformation types realized by him). The logical continuation of the investigations of the transformations of α-oxy-carbonyl compounds were his manifold papers on the monoses and disaccharides, as, for instance, those on a new method for the "epimerization" of sugars. He and his cooperators synthesized a large number of derivatives of multivalent alcohols, their aldehydes and monoses. Based on an intramolecular simultaneous acid-alkaline reaction process found by him in a large number of reactions he could explain many biochemical processes of nature. There is 1 table.

SOV/79-28-12-13/41

AUTHORS: Temnikova, T. I., Oshuyeva, N. A.

TITLE: Chemical Transformations of α-Halogen Ketones (Khimicheskiye prevrashcheniya α-galogenketonov) VI. Action of Sodium Phenolate and Cresylate on α-Bromo-Cyclohexanone (VI. Deystviye fenolyata i krezolyata natriya na α-bromtsiklogeksanon)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol 28, Nr 12, pp 3224-3226 (USSR)

ABSTRACT: Continuing earlier papers (Ref 1) this paper deals with the reaction of sodium phenolate and -p-cresylate with α-bromocyclehexanone in methyl alcohol solution. The problem was whether also in the cyclohexanone series the formation of mixed ketals could be found, which would indirectly point to the formation of phenyl "lactolides" in this series. Ebel (Ebel') (Ref 3) was the first to carry out this reaction in petroleum ether, and he obtained a product with the melting-point of 64-65°, of the empirical formula $C_{12}H_{14}O_2$. In the beginning he looked upon it as a phenoxy cyclohexanone, which, however, he later substituted for the phenoxy oxide, based on the hydrolysis with phenylhydrazine. The authors obtained again the same product following Ebel's method, with the only

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Chemical Transformations of α-Halogen Ketones. VI. Action of Sodium Phenolate and Cresylate on α-Bromo-Cyclohexanone

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difference that the sodium bromide was separated by centrifuging and not by water; this was done to avoid a decomposition of the phenyl "lactolide" to be expected. Ebel's product melting at 65° was spectrochemically investigated and its absorption spectra pointed to a carbonyl and phenyl group. Thus, the initial idea of Ebel (Formula I=α-phenoxy cyclohexanone) was proved, which could also be supported by the hydrolysis of the product with 2,4-dinitro-phenyl hydrazine, as opposed to the second idea, in the form of 2,4-dinitro-phenyl hydrazone. The reaction of sodium phenolate with α-bromo-cyclohexanone was no longer carried out in petroleum ether by the authors (according to Ebel), but in methyl alcohol, and they obtained the methyl-phenyl ketal of cyclohexanolon (II); this ketal is extremely unstable and requires special precaution in its distillation to obtain an analytically pure form. On the action of p-sodium cresylate on α-bromo-cyclohexanone in methyl alcohol also a highly unstable methyl-p-cresyl ketal of cyclohexanolon was obtained. There are 6 references, 3 of which are Soviet.

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Chemical Transformations of α-Halogen Ketones. VI. Action of Sodium Phenolate and Cresylate on α-Bromo-Cyclohexanone

SOV/79-28-12-13/41

ASSOCIATION: Leningradskiy gosudarstvennyy universitet (Leningrad State University)

SUBMITTED: December 31, 1957

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TEMNIKOVA, Tat'yana Ivanovna; KHAVIN, Z.Ya., red.; SHUR, Ye.I., red.; KHLIKH, Ye.Ya., tekhn.red.

[Theoretical fundamentals of organic chemistry] Kurs teoreticheskikh osnov organicheskoi khimii. Leningrad, Gos.nauchno-tekhn.izd-vo khim.lit-ry, 1959. 808 p. (MIRA 12:8)
(Chemistry, Organic)

SOV/79-29-2-7/71

AUTHORS: Temnikova, T. I., Kovalevskaya, R. N., Matveyenkova, N. I., Sklyarova, V. V.

TITLE: Investigation in the Field of Cyclic Acetals of Oxy-carbonyl Compounds (Issledovaniye v oblasti tsiklicheskikh atsetaley oksikarbonil'nykh soyedineniy). IX. Ethyl Lactolides and Diethyl Ketals of Ethyl-benzoyl Carbinol and Propyl-benzoyl Carbinol (IX. Etillaktolidy i dietilketali etilbenzoilkarbinola i propilbenzoilkarbinola)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 2, pp 381-386 (USSR)

ABSTRACT: Investigation of ethyl lactolides of the α-keto alcohols has been hitherto very scarce. Following up earlier papers by Temnikov and collaborators, as well as of other chemists, the present paper describes the synthesis of two new ethyl lactolides of the secondary aliphatic-aromatic α-keto alcohols, ethyl-benzoyl carbinol and propyl-benzoyl carbinol. On carrying out the reaction in the usual way, i.e. by the action of a suspension of sodium ethylate in absolute ether, resinification occurred:

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Investigation in the Field of Cyclic Acetals of Oxy-carbonyl Compounds. IX. Ethyl Lactolides and Diethyl Ketals of Ethyl-benzoyl Carbinol and Propyl-benzoyl Carbinol

$$C_6H_5\text{-}\underset{\underset{O}{\|}}{C}\text{-}CHBr\text{-}R \xrightarrow{C_2H_5ONa} C_6H_5\text{-}C(OC_2H_5)\text{-}O\text{-}CH\text{-}R$$

where $R=C_2H_5$ (II) or C_3H_7

Both ethyl lactolides (yield 10-15%) are very unstable and immediately yield ethyl-benzoyl carbinol with water in an alkaline medium. On the action of sodium ethylate upon the same bromoketones in absolute alcohol resinification is insignificant; still, only with α-bromo-butyl-phenyl ketone the separation of the corresponding lactolide (II, $R=C_3H_7$) was successful. On standing, however, either diethyl ketals of the corresponding α-keto alcohols (III) or further transformation products are formed. Thus, on the action of sodium ethylate on α-bromo-propyl-phenyl ketone not diethyl ketal is formed but a lactolide of ethyl-benzoyl carbinol (IV, $R=C_2H_5$). Diethyl ketals (III, $R=C_2H_5$ or n.-C_3H_7) are obtained at low temperature only. In analytically

Investigation in the Field of Cyclic Acetals of Oxy-carbonyl Compounds. IX. Ethyl Lactolides and Diethyl Ketals of Ethyl-benzoyl Carbinol and Propyl-benzoyl Carbinol

pure state only diethyl ketal of ethyl-benzoyl carbinol was obtained, which is likewise very unstable. Ethyl lactolides are much more unstable than methyl lactolides of the same keto alcohols. On the action of $ZnCl_2$ on the ethyl lactolide of propyl-benzoyl carbinol, a dimerization takes place in the cyclodiethyl dilactolide. There are 10 references, 6 of which are Soviet.

ASSOCIATION: Leningradskiy gosudarstvennyy universitet (Leningrad State University)

SUBMITTED: December 31, 1958

TEMNIKOVA, T. I.

Leningrad. Universitet

Voprosy teorii strogoniy organicheskikh soyedineniy (Problems in the Theory of the Structure of Organic Compounds) [Leningrad] 1960. 239 p. Errata slip inserted. 3,725 copies printed.

Sponsoring Agency: Leningradskiy ordena Lenina Gosudarstvennyy universitet im. A.A. Zhdanova.

Resp. Ed.: T.A. Favorskaya; Ed.: V.D. Platonov; Tech. Ed.: S.D. Yedelgina.

PURPOSE: This collection of articles is intended for chemists and organic chemists.

COVERAGE: The collection is concerned with the scientific legacy of A.Ye. Favorskiy, and includes discussions of his theoretical views and their evolution in connection with the development of theoretical organic chemistry. The articles present new problems on the structure, reactivity and transformations of various classes of organic compounds: unsaturated acyclic and cyclic hydrocarbons, saturated and unsaturated alcohols, glycols and carbonyl compounds. No personalities are mentioned. References accompany each article.

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78257
SOV/79-30-3-11/69

AUTHORS: Temnikova, T. I., Gissel', R., Gontarev, B. A.

TITLE: Investigation in the Field of Cyclic Acetals of Oxycarbonyl Compounds. X. Methyl Lactolides of Dimethyl--p-Anisoyl- and Dimethyl-p-Chlorobenzoyl Carbinols and Their Transformations

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol 30, Nr 3, pp 776-781 (USSR)

ABSTRACT: Two methyl lactolides of tertiary aliphatic-aromatic α-keto alcohols with Cl- and CH_3O-substituted benzene ring were synthesized. α-bromoisopropylanisyl ketone (I, X = CH_3O) on slow heating with sodium methylate gave an oily substance, which, on vacuum distillation and fractionation, gave the methyl lactolide of dimethyl-p-anisoyl carbinol (II, X = CH_3O; bp 84° C at 2 mm; 97° C at 4 mm; 108.5° C at 6 mm; mp 38.5-39° C).

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Investigation in the Field of Cyclic Acetals of Oxycarbonyl Compounds. X

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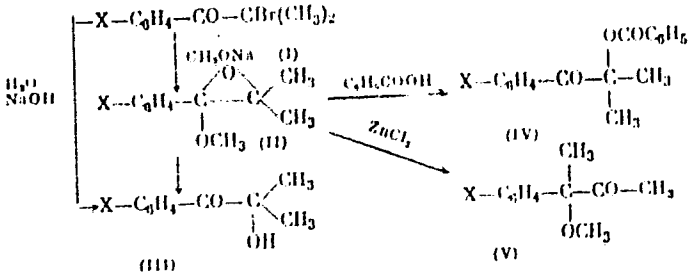

Methyl lactolide of dimethyl-p-chlorobenzoyl carbinol (II, X = Cl, bp 94-95° C at 5 mm) was obtained similarly from α-bromoisopropyl-p-chlorophenyl ketone (I, X = Cl). Both lactolides were comparatively stable and did not decompose in sealed ampoules for a long period of time. They were hygroscopic and hydrolized in air forming the corresponding α-keto alcohols (III). The methoxy--substituted lactolide was much more hygroscopic and hydrolized more easily than the chlorine-substituted

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Investigation in the Field of Cyclic Acetals of Oxycarbonyl Compounds. X

(USSR)
SOV/79-30-5-11/69

one. The lactolides in reaction with benzoic acid gave the corresponding esters (IV; mp 73.5-74.5° C, from petroleum benzin, for X = CH_3O, mp 110-111° C, from aqueous methanol, for X = Cl). Heating with a small amount of $ZnCl_2$ isomerized the lactolides into the corresponding methoxy ketones (V, bp 10?-10?° C at ?.5 mm; mp 41-42° C, for X = CH_3O; bp 118-119° C at 9 mm for X = Cl). Carbinol (III, X = CH_3O, mp 54-55° C) was also obtained on heating the bromoketone I with aqueous NaOH or on hydrolysis of the methyl lactolide with 5% H_2SO_4, also with heating. The introduction of Cl-substituent in para-position of the benzene ring speeded up the reactions as compared with unsubstituted or CH_3O--substituted compounds. The bromoketone (I, X = Cl) gave with NaOH a highly exothermal reaction yielding carbinol (III, X = Cl, bp 115-117° C). The latter

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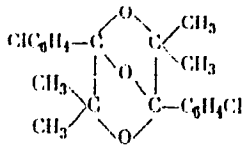
was very unstable and in the presence of acids was transformed into the anhydrodimer (VI, mp 177-178° C, from aqueous methanol) of a presumably tricyclic structure.



(VI)

There are 9 references, 2 U.S., 1 German, 6 Soviet. The U.S. references are: P. Z. Bayless, C. R. Hauser, J. Am. Chem. Soc., 76, 2306 (1954); A. K. Glasgow, G. Ross, J. Res. NBS, 57, Nr 5 (1956).

ASSOCIATION: Leningrad State University (Leningradskiy gosudarstvennyy universitet)

SUBMITTED: July 22, 1959

TEMNIKOVA, T.I.; GONTAREV, B.A.; GISSEL', R.

Cyclic acetals of hydroxy carbonyl compounds. Part 11: Interaction between methyl lactolides of fatty-aromatic δ-keto alcohols and aromatic aldehydes and ketones. Zhur.ob.khim. 30 no.8: 2457-2462 Ag '60. (MIRA 13:7)

1. Leningradskiy gosudarstvennyy universitet.
(Aldehydes) (Ketones) (Alcohols)

TEMNIKOVA, T.I.; CHERKASOVA, V.A.; PIASTRO, V.D., red.; KISELEVA, L.I., tekhn. red.

[Reference literature on organic chemistry] Spravochnaia literatura po organicheskoi khimii. Leningrad, Izd-vo Leningr. univ., 1961. 90 p. (MIRA 15:1)
(Bibliography--Chemistry, Organic)

TEMNIKOVA, T.I.; YERSHOV, B.A.

Reactions of sodium acetoacetate with α-oxybromides. Zhur.ob. khim. 31 no.7:2435-2436 Jl '61. (MIRA 14:7)

1. Leningradskiy gosudarstvennyy universitet imeni A.A. Zhdanova.
(Acetoacetic acid) (Bromides)

TEMNIKOVA, Tat'yana Ivanovna; KHAVIN, Z.Ya., red.; SHUR, Ye.I., red.; ERLIKH, Ye.Ya., tekhn. red.; FOMKINA, T.A., tekhn. red.

[Course in the theoretical principles of organic chemistry] Kurs teoreticheskikh osnov organicheskoi khimii. Izd.2., perer. i dop. Leningrad, Goskhimizdat, 1962. 948 p. (MIRA 16:1)

(Chemistry, Organic)

TEMNIKOVA, T.I.; TAKHISTOV, V.V.

Exchange reactions of ketals of aromatic ketones. Zhur.VKHO 7 no.1:115-116 '62. (MIRA 15:3)

1. Leningradskiy gosudarstvennyy universitet.
(Acetals) (Ketones)

TEMNIKOVA, T.I.; OSHUYEVA, N.A.

Interaction of β-hydroxy aldehydes with methyl alcohol. Zhur.-VKHO 7 no.2:233-234 '62. (MIRA 15:4)

1. Leningradskiy gosudarstvennyy universitet.
(Aldehydes) (Methanol)

TEMNIKOVA, T.I., prof.

Structure of molecules and molecular rearrangements. Zhur. VKHO 7 no.4:427-435 '62. (MIRA 15:8)
(Chemical structure) (Rearrangements (Chemistry))

TEMNIKOVA, T.I.; YERSHOV, B.A.

Reactions of methylbenzoylcarbinol and ethylbenzoylcarbinol methyllactolides with sodium acetoacetic ester. Zhur.ob.khim. 32 no.2:661-662 F '62. (MIRA 15:2)

1. Leningradskiy gosudarstvennyy universitet.
(Alcohols)
(Acetoacetic acid)

TEMNIKOVA, T.I.; YERSHOV, B.A.

Interaction of metal derivatives of β-dicarbonyl compounds with α-halogen oxides. Part 1: Interaction of Na- and $C_6H_5CH_2(CH_3)_3N^+$ derivatives of acetoacetic ester with α-bromine oxides of isomeric butenes. Zhur.ob.khim. 32 no.8:2436-2442 Ag '62. (MIRA 15:9)

1. Leningradskiy gosudarstvennyy universitet.
(Acetoacetic acid) (Butene) (Bromine oxide)

TEMNIKOVA, T.I.; OSHUYEVA, N.A.

β-Hydroxy- and β-halo carbonyl compounds. Part 2: Preparation of aliphatic-aromatic β-ketols substituted in the nucleus. Zhur. ob. khim. 33 no.5:1403-1404 My '63.
(MIRA 16:6)

1. Leningradskiy gosudarstvennyy universitet.
(Carbonyl compounds)

TEMNIKOVA, T.I.; YERSHOV, B.A.

Reactions of metallic derivatives of β-dicarbonyl compounds with α-halooxides. Part 2: Reaction of Na-dimedon with α-bromooxides of isomeric butenes and with epibromohydrin. Zhur. ob. khim. 33 no.5:1405-1408 My '63. (MIRA 16:6)

1. Leningradskiy gosudarstvennyy universitet.
(Cyclohexanedione) (Butene)
(Epibromohydrin)